GEOCHEMISTRY

A Translation of

ГЕОХИМИЯ

CONTENTS

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TRANSLITERATION

There is no ideal system of transliterating Russian; each has its advantages and disadvantages. For the translation of Geokhimiya we have chosen the system used by Chemical Abstracts, partly because of its wide acceptance by other journals and partly because of certain advantages in alphabetization of names. The principal differences between this system and others in common use are as follows:

Russian	Chem. Abs.	Others
X	kh	h
Ц	ts	tz
Щ	shch	sch
Ю	yu	iu
Я	ya	ia

THE IMMEDIATE PROBLEMS
OF GEOCHEMISTRY

The proposals presented by N. S. Khrushchev at the XXI Congress of the Communist Party of the Soviet Union confront our science with a number of very important problems.

The projected schedule provides for an accelerated development of ferrous metallurgy and especially of the reserves of its raw material, iron ore.

In 1965 it is planned to smelt 65-70 million tons of pig iron, an increase of 65-77% over 1958, to produce 86-91 million tons of steel, an increase of 56 to 65%, to produce 65-70 million tons of rolled steel, an increase of 52 to 64%, and to stockpile 150-160 million tons of iron ore (230-245 million tons of crude ore).

It is planned also to increase the production of aluminum 2.8 times and of refined copper, 1.9 times as compared with 1958 and to increase considerably the production of nickel, magnesium, titanium, germanium and silicon. The production of other nonferrous metals and especially of rare metals will also be increased.

The schedule calls for an accelerated development of the chemical industry. Its total output is to be increased almost three times.

The role of oil and gas in the total production of fuel will be increased from 31% at present to 51% in 1965, and the role of coal decreased from 59% to 43%.

In order to hasten the development of the productive forces of the country and to provide raw materials for the planned growth of the national economy, it is intended to increase geological exploratory work by 65%.

Soviet geochemistry is confronted with important problems in connection with these plans.

Geochemistry is concerned directly and in a practical way with the study of mineral raw materials, with the search for new sources of these materials, with increasing our mineral resources as a whole and those of rare and nonferrous metals in particular, and with the manifold utilization of these raw materials in the development of metallurgy, technology, agriculture, medicine, etc.

Minerals, rocks and ores are products of chemical processes occurring in the earth's crust. These processes cause either concentration or dispersion of the elements. During the past 25 years, geochemists have achieved notable success in the study of natural processes by the use of modern physical and chemical methods of investigation.

Only recently geology has acquired and adopted radioactive methods of determining the absolute age of minerals and rocks, methods of

determining the temperature and other conditions of formation of rocks and minerals by the isotopic composition of Pb, O, S and C, the method of measuring the temperatures of the ancient seas or paleothermometry, based on the content of O^{18}, etc. The method of prospecting for ores by studying dispersion aureoles is being developed on a large scale.

The use of gamma-logging in the search for petroleum, boron and other elements was followed by the introduction of neutron logging.

The study of distribution of rare elements in the individual minerals of rocks as indicators of petrogenetic processes has become extremely important. These and other investigations have amassed new data which will serve as a basis for geochemical criteria applicable to the search for ore and in particular for deposits of rare and dispersed elements. These achievements of science are of great practical importance and are the work of numerous geochemists. A considerable part of this work was done by Soviet geochemists.

There is no doubt that these investigations must be expanded in view of the new problems arising before the science.

Undoubtedly one of the most important problems is the discovery of the pattern of regional distribution of the elements. The irregularity of their distribution is the result of a complex of processes. The study of the distribution of the elements, and especially of ore deposits, beneath the surface of the earth requires application of geophysical and geochemical methods. The latter cannot be developed without a knowledge of geochemical processes. The nature of these processes is usually deduced from the final products, minerals and rocks, but this is not enough and does not provide complete information. More physicochemical research is needed in geochemistry with equal attention given to theory and experiment. New ideas and profound generalizations in geochemistry, as in many other sciences, grew out of new experimental data, and experiments with the use of refined techniques must take an important place in geochemical research.

At the same time, work in regional geochemistry must be expanded in a close association with metallogenetic investigations. This subject has not received sufficient attention in our country in recent years. Yet good monographs on regional geochemistry of Siberia, Middle Asia, the Far East and other territories are much needed. Without comparison between modeled processes and regional geochemical data, the problem of the distribution of the elements cannot be viewed against the background of all other geological data and will remain unsolved. The investigators' efforts must be directed not only to the acquisition of exact knowledge of individual chemical processes, and especially those which take place at depth in the earth's crust, but also to their classification and systematization.

Another, no less important problem is the acquisition of the most complete knowledge possible of individual elements, especially rare ones such as niobium, tantalum, germanium, zirconium, boron, beryllium, uranium and others, because the need for these elements is growing in the national economy. Exact quantitative data on the occurrence of trace elements in nonferrous and ferrous metals (ores) may lead to the discovery of new complex sources of rare and dispersed elements. The by-products of our beneficiation and metallurgical plants may also turn out to be sources of these elements.

The form of occurrence of individual elements in minerals, rocks and ores and the mode of their migration are serious geochemical problems. Studies of the distribution of rare elements in the rock-forming minerals, based on crystal chemistry, are needed. Such studies, together with

isotope geology, promise to clarify the relation between ore deposits and igneous rocks, a problem which is occupying many geologists. These researches will undoubtedly make new contributions to the subject of ore genesis.

Investigations of the physiochemical principles of the processes within the earth's crust must serve as the basis for discovering new geochemical guides to the deposits of various useful minerals. The search for ore is one of the most practical applications of geochemistry. Inasmuch as gas and petroleum will be particularly important as raw materials for the production of synthetics and objects satisfying the needs of the whole national economy, it is necessary to accelerate work in the field of geochemical evaluation of petroleum content of rocks and to further the development of methods of exploration by means of gas anomalies by applying modern methods of refined differential analysis of natural gases. The already tested geochemical methods of prospecting for gas and petroleum are aiding substantially in the search for new fields and will continue to do so.

Besides aiding in gas and petroleum exploration, geochemical methods must play a large role in the search for deposits of many other minerals and, what is especially important, deposits which do not outcrop at the surface and cannot be discovered by the usual geological methods. At present it is generally accepted that such "hard to find" deposits are many and contain great potential reserves of different ores. These reserves are several times as great as those in the exposed deposits, which until recently have been the main objectives of prospectors and exploration geologists. The problem of searching for deep-seated deposits becomes more and more vital every year. Together with other methods, the geochemical methods of prospecting will play an important role in this search.

The search for the rare and dispersed elements is quite impossible without geochemical data. The numerous and varied quantitative methods of determination of individual rare elements must be adopted as much as possible to use in the field together with other methods of prospecting for rare elements.

The geochemist will play an important role in the geological service. He will obtain exact quantitative data on the composition of materials and use them in guiding exploration. He will evaluate discovered mineral deposits, especially with reference to the associated minor elements. He will help in the solution of technological problems by pointing out possible manifold uses of raw materials.

This will require continuous improvement in the teaching of geochemistry in the institutions of higher learning. A geochemist may be trained either in a department of geology or of chemistry. In our country in a number of universities geochemists are trained in departments of geology. The basis of their knowledge however, must be a sound and practical knowledge of physical chemistry, and this must be stressed in the curricula.

There are in our country institutions devoted to the solution of geochemical problems and laboratories where particular geochemical problems are investigated. This is not enough. The experimental work providing a basis for the development of general geochemical theory must be expanded, for without it the science cannot advance. Descriptive work should be superceded by the application of thermodynamic and physicochemical laws to the explanation of the observed patterns of distribution of elements in a given natural process. More problems dealing with mineral exploration should be undertaken in geochemical institutes and laboratories.

It is planned to develop geochemical research in the Siberian Affiliate of

the Academy of Sciences and to organize a geochemical institute in Irkutsk. But this is not enough. It is necessary to broaden geochemical investigations in the different geological organizations of the country. The level of development of geochemistry must satisfy the great demands of the national economy, and Soviet geochemists must exert all possible effort to fulfill the grandiose program of economic development of the USSR during the coming seven years.

TRANSPORTATION OF URANIUM
IN HYDROTHERMAL SOLUTION
AS A CARBONATE

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In the most widely held of the various hypotheses concerning the mode of transportation of uranium in hydrothermal solutions, it is assumed that uranium is transported in the form of a carbonate. The hypothesis is based on the observation that most uranium-bearing natural springs have high carbon dioxide content and on experimental data indicating high solubility of hexavalent uranium in carbonated aqueous solutions [1]. Moroever, in an overwhelming majority of vein uranium deposits, pitchblende is associated with widely developed carbonates of many kinds [2]. The signs of oxidation-reduction reactions (hematitization of the enclosing rocks and reaction relationships with earlier minerals) and the absence of thorium, an element diadochic with quadrivalent uranium, from the hydrothermal uraninite veins suggest that uranium was transported in the solutions in hexavalent form and was reduced only at the time of deposition.

In the present work an attempt is made to approach this question from the physicochemical point of view, and afterwards compare the data with the basic geological knowledge.

Hexavalent uranium forms stable uranyl carbonate compounds in aqueous carbonate solutions. It now may be considered as proved that two complex uranyl carbonate anions exist in aqueous solutions: uranyl bicarbonate $UO_2(CO_3)_2 \cdot (H_2O)_2]^{2-}$, and uranyl tricarbonate $[UO_2(CO_3)_3]^{4-}$. The existence in aqueous solutions of anions with other proportions of uranium and carbon is debatable. Without entering into the substance of this debate, it must be pointed out that convincing data [3] recently have appeared which point to the existence of a single genetic series:

$$[UO_2(CO_3)_3]^{4-}; \quad [(UO_2)_2(CO_3)_5(H_2O)_2]^{6-}; \quad [UO_2(CO_3)_2(H_2O)_2]^{2-};$$
$$[(UO_2)_2(CO_3)_3(OH)(H_2O)]^{3-}_8; \quad [UO_2(CO_3)(OH)(H_2O)_3]^{1-}.$$
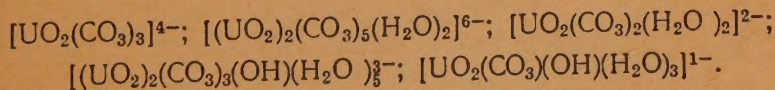
However, in dilute water solutions in the state of equilibrium, the concentration of the complex uranyl carbonate anions with the C/U ratio other than 2 and 3 will be negligible as compared with the concentration of uranyl bi- and tricarbonates [3, 4, 5, 6]. It is precisely these two characteristic

compounds that will determine the specific behavior or uranium in hydro-thermal solutions.

In order to obtain a general idea of the behavior of hexavalent uranium in aqueous carbonate solutions, it is useful to review the conditions of equilibrium between its different compounds. These conditions may be characterized in a general way by simple calculations based on the princi-ples of physical chemistry. The most general relationships discovered in this way can be made specific for certain temperatures, pressures and concentrations and can be checked experimentally.

Theoretical Calculations

The equilibrium in the system uranyl tricarbonate -- uranyl hydroxide may be represented as follows:

$$[UO_2(CO_3)_3]^{4-} \rightleftarrows UO_2^{2+} + 3CO_3^{2-}.$$
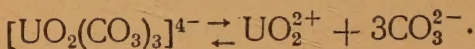
This equilibrium is determined by the equilibrium constant (instability constant) of the complex:

$$\frac{[UO_2^{2+}][CO_3^{2-}]^3}{[UO_2(CO_3)_3^{4-}]} = K_1.$$

Here and below, concentrations (expressions in square brackets) will be used instead of activi-ties, assuming that the activity coefficient $f = 1$. In the case of dilute solutions, this assumption does not lead to significant error and is widely used.

It can be seen from the expression for the instability constant of the complex that the ratio of the concentration of free uranyl ions to the con-centration of the uranyl bound in the complex is inversely proportional to the third power of concentration of free CO_3^{2-} ions. If the concentration of free CO_3^{2-} ions is increased, the equilibrium shifts towards the formation of a complex anion, and vice versa. Obviously, in the solution containing uranyl tricarbonate, part of the uranium is present in the complex anion and part in the form of free uranyl ions. $[UO_2^{2+}] + [UO_2(CO_3)_3^{4-}] = C_U$, where C_U is the total concentration of uranium in the solution. Substituting this symbol in the expression for the instability constant, and solving for $[UO_2^{2+}]$, we obtain:

$$[UO_2^{2+}] = \frac{K_1 C_U}{[CO_3^{2-}]^3 + K_1}.$$

This equation shows that the concentration of free uranyl ions increases with increase in the total uranium concentration and decreases with increase in the concentration of free CO_3^{2-} ions. Increase in the concentration of UO_2^{2+} ions may bring about hydrolysis according to the equation:

$$UO_2^{2+} + 2OH^- \rightleftharpoons UO_2(OH)_2.$$
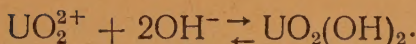
The products of hydrolysis of the uranyl ion have a complex composition represented by the general formula $nNa_2UO_4 \cdot mUO_3 \cdot lH_2O$ where the n/m ratio depends on the pH of the surrounding medium. Sutton's investigations [7] have shown that at pH <7, $n/m < 1/15$, which corresponds to the formula $Na_2U_{16}O_{49}$ and only at pH >10, n/m becomes equal to one, which corresponds to sodium diuranate, $Na_2U_2O_7$. For the sake of simplicity, we consider only one product of hydrolysis of the uranyl ion, the hydroxide $UO_2(OH)_2$, remembering that as the pH value of the medium increases, compounds more and more enriched in Na form, approaching $Na_2\overline{U}_2O_7$, in composition.

The conditions of equilibrium between the products of hydrolysis of the uranyl ion and the UO_2^{2+} ions are determined by the solubility product $[UO_2^{2+}][OH^-]^2 = K_2$. Transforming this equation and substituting $[H^+]$ for $[OH^-]$, we have $[UO_2^{2+}] = \dfrac{K_2[H^+]^2}{K_W^2}$, where K_W is the ionization constant of water.

Evidently under the conditions of equilibrium the concentrations of the uranyl ions determined by the dissociation of the hydroxide and of the uranyl carbonate complex will be equal, and therefore

$$[UO_2^{2+}] = \frac{K_2[H^+]^2}{K_W^2} = \frac{K_1 C_U}{[CO_3^{2-}]^3 + K_1} .$$

Solving this equation for CO_3^{2-}, we find:

$$[CO_3^{2-}] = \sqrt[3]{\frac{K_1(K_W^2 C_U - K_2[H^+]^2)}{K_2[H^+]^2}} . \qquad \text{(Ia)}$$

This is an expression for the relation between the concentrations of uranium, CO_3^{2-} ions and the pH value of the solution containing uranyl tricarbonate.

The concentration of the free CO_3^{2-} ions, in turn, is definitely related to the remaining forms of carbon dioxide dissolved in water ($\Sigma' CO_2$) and, in the final analysis, for a given P and t, it is determined by the pH value and the partial pressure of carbon dioxide, P_{CO_2}. The dependence of the concentration of the free CO_3^{2-} ions on the total concentration of carbon dioxide dissolved in water may be expressed as follows:

$$\Sigma' CO_2 = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3];$$

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_5; \quad \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = K_6,$$

where K_5 and K_6 are, respectively, the first and second dissociation constants of carbonic acid. Solving this system of equations for CO_3^{2-}, we find:

$$[CO_3^{2-}] = \frac{\Sigma'CO_2 K_5 K_6}{K_5 K_6 + K_5[H^+] + [H^+]^2} \; .$$

Denoting $\dfrac{K_5 \cdot K_6}{K_5 K_6 + 5K_5[H^+] + [H^+]^2}$ by A, we get:

$$[CO_3^{2-}] = \Sigma'CO_2 A. \tag{II}$$

If P and t are given, $A = f[H^+]$, the values of A for different pH values may be computed and used in all further calculations. Substituting the expression obtained for CO_3^{2-} in the equation (Ia), we obtain:

$$\Sigma'CO_2 = \frac{1}{A} \sqrt[3]{\frac{K_1 (K_W^2 Cu - K_2 [H^+]^2)}{K_2[H^+[^2}} \tag{Ib}$$

The dependence of $[CO_3^{2-}]$ on P_{CO_2} and pH may be expressed in the following manner. The relation between the gaseous CO_2 and that dissolved in water, $CO_{2\,(gas)} \rightleftharpoons CO_{2\,(sol.)}$, is determined by the constant:

$$\frac{[H_2 CO_3]}{P_{CO_2}} = K_7.$$

Solving this equation together with the equations of the first and second stages of dissociation of carbonic acid, we have:

$$[CO_3^{2-}] = \frac{P_{CO_2} K_5 K_6 K_7}{[H^+]^2} \; . \tag{III}$$

Substituting in equation Ia, we find that:

$$P_{CO_2} = \frac{[H^+]^2}{K_5 K_6 K_7} \sqrt[3]{\frac{K_1 (K_W^2 Cu - K_2[H^+]^2)}{K_2 [H^+]^2}} \; . \tag{Ic}$$

We have now a general analytical expression for the conditions of equilibrium between uranium hydroxide and the solution containing the uranyl tricarbonate anion. These equations are most easily treated graphically, and this will be done below. It can be seen that equation (Ic) has a meaning

if $K^2_W C_U \gg K_2[H^+]^2$ or if $C_U \gg \dfrac{K_2}{[OH^-]^2}$; i.e., the equation is meaningless for pH values lower than the pH of the hydrolysis of the uranyl ion for each concentration of uranium.

An analytical expression of the conditions of equilibrium for other uranyl compounds is derived in a similar way:

$$[UO_2(CO_3)_2]^{2-} + 2OH^- = UO_2(OH)_2 + 2CO_3^{2-}$$

$$[CO_3^{2-}] = \sqrt{\frac{K_3(K^2_W C_U - K_2[H^+]^2)}{K_2[H^+]^2}}, \qquad (IV)$$
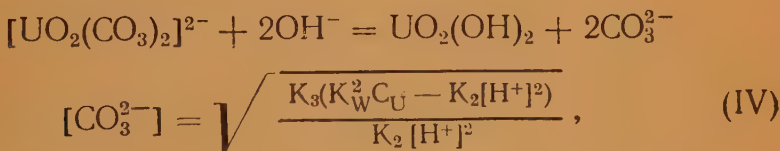
where K_3 is the instability constant of the uranyl bicarbonate complex.

$$[UO_2(CO_3)_3]^{4-} = [UO_2(CO_3)_2]^{2-} + CO_3^{2-}$$

$$[CO_3^{2-}] = \frac{K_1}{K_3} \cdot \qquad (V)$$

$$[UO_2(CO_3)_2]^{2-} = UO_2CO_3 + CO_3^{2-}$$

$$[CO_3^{2-}] = \frac{K_3 C_U + \sqrt{K_3^2 C_U^2 - 4K_3 K_4^2}}{2K_4}, \qquad (VI)$$
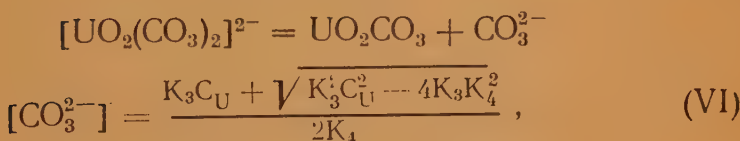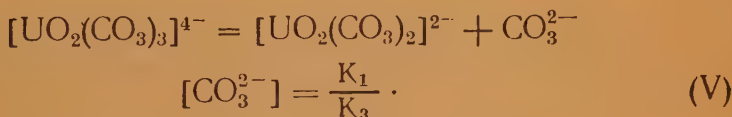
where K_4 is the solubility product of uranyl monocarbonate.

$$UO_2CO_3 + 2OH^- = UO_2(OH)_2 + CO_3^{2-}$$

$$[CO_3^{2-}] = \frac{K_4 K^2_W}{K_2[H^+]^2} \cdot \qquad (VII)$$

$$UO_2(OH)_2 = UO_2^{2+} + 2OH^-$$

$$[H^+] = \sqrt{\frac{C_U K^2_W}{K_2}} \cdot \qquad (VIII)$$

$$UO_2CO_3 = UO_2^{2+} + CO_3^{2-}$$

$$[CO_3^{2-}] = \frac{K_4}{C_U} \cdot \qquad (IX)$$
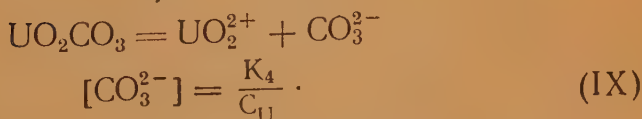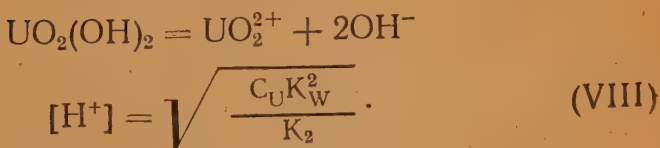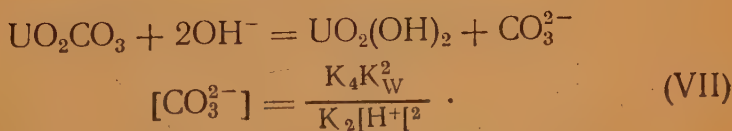
It is not at all difficult now to obtain the values of P_{CO_2} and $\Sigma' \, CO_2$ instead of $[CO_3^{2-}]$ by substituting in these equations the values of $[CO_3^{2-}]$ from equations (II) and (III). If the value of the equilibrium constant for a definite P and t is substituted in any of the equations, the conditions of equilibrium will have numerical expression. Unfortunately, the required

constants are known at present only for room temperature and normal pressure. Even the data for their extrapolation into the regions of higher temperature are inadequate. Therefore, before passing on to experiments at elevated temperatures, attention must be given to the relations at room temperature.

Behavior of Uranyl Carbonates at Room Temperature

Figs. 1a and b show the stability fields of the uranium compounds under discussion in the coordinates pH and log P_{CO_2} for uranium concentrations of 10^{-2} and 10^{-3} mole/l. The boundaries were computed by means of the equations of equilibrium derived above, and correspond in the case of
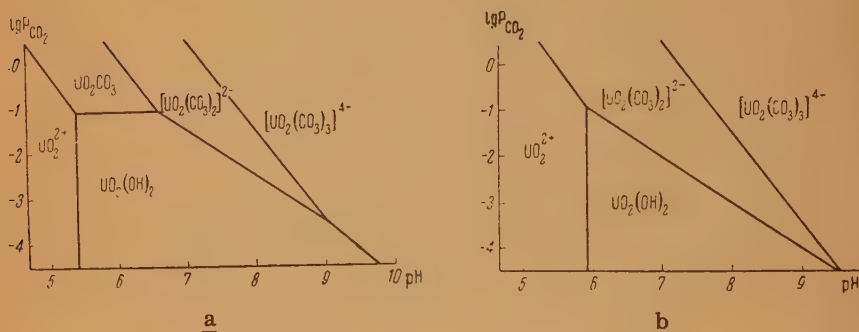
Fig. 1. Dependence of the stability fields of uranyl compounds on the acidity of the medium and partial CO_2 pressure, t = 25°C.
a -- C_U = 10^{-2} mole/l, b -- C_U = 10^{-3} mole/l.

change from one solution into another, to equal concentration of the two types of ions, and in the case of change from solution to solid phase, to the beginning of formation of the solid phase. The numerical values of the equilibrium constants are given in the table.

Equation	Con-stant	Num. value	Ref.	Equation	Con-stant	Num. value	Ref.
$[UO_2(CO_3)_3]^{4-} =$ $= UO_2^{2+} + 3CO_3^{2-}$	K_1	$10^{-18,3}$	[4]	$H_2CO_3 = H^+ + HCO_3^-$	K_5	$10^{-6,43}$	[9]
$UO_2(OH)_2 = UO_2^{2+} +$ $+ 2OH-$	K_2	$10^{-19,2}$	[8]	$HCO_3^- = H^+ + CO_3^{2-}$	K_6	$10^{-10,24}$	[9]
$[UO_2(CO_3)_2]^{2-} =$ $= UO_2^{2+} + 2CO_3^{2-}$	K_3	$10^{-14,7}$	[4]	$CO_{2 (gas)} = CO_{2 (sol.)}$	K_7	$10^{-1,5}$	[10]
$UO_2CO_3 = UO_2^{2+} + CO_3^{2-}$	K_4	$10^{-10,5}$	*	$UO_2 + 2H_2O = U^{4+} +$ $+ 4OH-$	K_8	10^{-52}	[11]

*Calculated from the values of the free energies of formation.

Note: Comma represents decimal point.

It can be seen from Figs. 1a and b that, as the alkalinity of the solution increases, the partial pressure of carbon dioxide required for the formation of the uranyl carbonate compounds diminishes rapidly. The boundary between the fields UO_2^{2+} and $UO_2(OH)_2$ does not depend on P_{CO_2}. The transformation of the uranyl monocarbonate into uranyl hydroxide (Fig. 1a) does not depend on the pH value. Equations (VII) and (III) show that the P_{CO_2} of this transformation does not depend on the concentration of uranium but only on the values of the equilibrium constants. For the conditions under discussion, the value of P_{CO_2} will be $10^{-1\cdot1}$ atm. in all cases. When the partial carbon dioxide pressure is lower than this value, it is impossible to obtain uranyl monocarbonate; when it is greater, the hydroxide cannot form. The partial carbon dioxide pressure in the air is less than this value, and therefore we cannot obtain uranyl monocarbonate precipitate by titrating uranyl carbonate solutions with acid in air. The field of the uranyl monocarbonate in Fig. 1b is absent altogether. To find the minimum uranium concentration at which the solid phase UO_2CO_3 will form, we use equation (IV). This equation shows that $K_3 C_U^2 \geqslant 4K_4^2$, or after substitution of numerical values, that $C_U \geqslant 10^{-2\cdot9}$.

The value for the concentration of uranium, $10^{-2\cdot9}$ mole/l, is the minimum value necessary for the formation of uranyl monocarbonate at P = 1
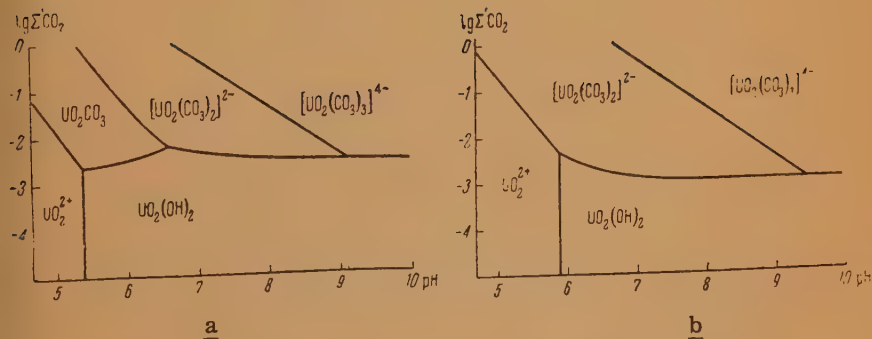
Fig. 2. Dependence of stability fields of uranyl compounds on the acidity of the medium and the total CO_2 in solution t = 25° C.
a -- $C_U = 10^{-2}$ mole/l, b -- $C_U = 10^{-3}$ mole/l.

atm. and t = 25° C. With increased uranium concentration, the uranyl monocarbonate field expands along the pH axis but remains unchanged along the P_{CO_2} axis.

All these conditions ($C_U = 10^{-2\cdot9}$ mole/l; $P_{CO_2} = 10^{-1\cdot1}$ atm., weakly

acid or neutral medium) substantially limit the possibility of formation of simple uranyl carbonates in nature. It is evidently not an accident that rutherfordine and its hydrous varieties are rare in nature. This group of minerals usually develops after primary uranium minerals, mainly in the upper zone of cementation (zone of mixed ores) directly below the water table [12], i.e., under conditions where local increase in uranium concentration may occur at the expense of primary uranium ores and elevated partial pressure of carbon dioxide resulting from the decomposition of primary carbonates. The medium in this case will be weakly acid or neutral.

The fields of stability of the uranyl compounds as functions of the acidity of the solution (pH) and the value of the total concentration of carbon dioxide ($\Sigma'\ CO_2$) in the solution are shown in Figs. 2a and b for uranium concentrations of 10^{-2} and 10^{-3} mole/l.

The diagrams show that for sufficiently large $\Sigma'\ CO_2$ different uranyl carbonates are stable over a broad pH range. In the same pH interval a decrease in $\Sigma'\ CO_2$ leads to the destruction of the uranyl compounds and formation of hydroxide. It is interesting to note that the equilibrium curve between the uranyl carbonate complexes and uranyl hydroxide slopes very slightly towards the pH axis. Indeed, increase in the pH of the solution leads, on the one hand, to an increase in the concentration of the OH⁻ ions which shift equilibrium towards the formation of hydroxide, and, on the other hand, towards the formation of uranyl carbonate complexes.

It was noted above that in an alkaline medium the products of hydrolysis of the uranyl ion have a more complex composition than uranium hydroxide. Naturally, the values of constant K_2 will also change in this region, and this will cause a change in the slope of the equilibrium curve. However, even if the constants change by several orders, the general picture is not changed.

Thus, in the alkaline region, within a broad interval of pH values, the main factor affecting the precipitation of uranium from the solution is the total concentration of carbon dioxide ($\Sigma'\ CO_2$). The change to the acid region results either in the formation of uranyl carbonate when the values of C_U and $\Sigma'\ CO_3$ are sufficiently large, or to the formation of free uranyl ions from all of the uranium present.

The Temperature of Formation of Pitchblende Veins

All of the relations derived above are based on the thermodynamic constants for an aqueous solution at t = 25°C and P = 1 atm.

Obviously, hydrothermal deposits may have formed at higher temperature and pressure. As has already been mentioned, we cannot, at present, evaluate the constants which interest us for other than standard conditions. But we are more interested in the change in the mutual relationship between the constants rather than in the change in their values, and, moreover, even if the latter change greatly, the relative position of the stability fields of our compounds is not affected, as can be seen from the above diagrams constructed on the logarithmic scale.

Owen and Brinkey [13] showed that for ionic equilibria the effect of total pressure may be disregarded.

It is more difficult to determine the limits to which the data for room temperature may be safely extrapolated into the region of elevated temperatures. Barton [10], using Van't Hoff's equation and certain assumptions,

extrapolated some of the equilibrium constants to 200°C. His data show that, in this temperature range, the main regularities characteristic for standard temperatures may be expected to be preserved. His assumptions, however, require experimental proof.

What are the actual temperatures of the processes under discussion?

In a number of hydrothermal uranium deposits, native bismuth is associated with pitchblende. The melting temperature of bismuth is 271°C at 1 atm., and as the pressure increases, it does not increase, but decreases. Thus, the temperature of formation of an association including native bismuth cannot exceed 271°C. In a number of deposits goethite is found among other iron oxides associated with pitchblende. It has been shown by Smith and Kidd [14] that the upper stability limit of this mineral depends on the alkalinity of the surrounding medium. For 0.1 $\underline{N}$ HCl solution, it lies at t = 100°C; for 0.1 $\underline{N}$ NaOH solution, at t = 160°$\overline{C}$. Pressure has almost no effect on the transition point (at $\Delta P = \pm 1000$ atm., $\Delta t = \pm 5°$). Finally, pitchblende itself is a compound with a variable composition, UO_n, where n is usually greater than 2. After a study of uranium oxides in the range $\overline{U}O_2$ -- U_3O_8, Perio [15] concluded that the region of compounds of variable composition with the structures and parameters of UO_2 (corresponding to natural pitchblendes) extends to 140°C. In the region of higher temperatures, the compound UO_2 is stable in mixtures with other uranium compounds of constant composition.

These data indicate that the temperature of formation of hydrothermal uranium deposits where uranium occurs in the form of pitchblende does not exceed 150°C and in many cases may be lower.

Experimental Data

In passing to experimental verification of the conditions of stability of the complex uranyl carbonate anions at elevated temperatures and pressures, it should be stated that the existence of these compounds under conditions different from standard is beyond doubt.

In any technological scheme for leaching of uranium from ores by the carbonate method, uranium is fixed in the carbonate complex at an elevated temperature. Usually the temperature of the process ranges from 90 to 120°C [16].

However, in all technological processes, these complexes exist in a highly concentrated soda solution. The behavior of the complexes in dilute soda solutions at elevated temperatures and the effect of carbon dioxide pressure and the concentration of the alkali metals are still little known.

Our experiments in establishing the stability boundaries for the uranyl carbonate anions at elevated P and t were made in a steel bomb with an inner quartz container. The working volume was 470 ml. A definite amount of sodium uranyl carbonate solution and titrated soda solution was placed in the quartz container and the volume was brought to 15 ml with distilled water.

In each series of experiments, the initial volume of the liquid phase and the concentration of uranium in it remained constant. The air was removed from the bomb by a stream of CO_2 from a cylinder. After this, the necessary carbon dioxide pressure was established in the bomb. The charged bomb was heated in a furnace to 150°C and maintained at this temperature or 6 hours. It took 12 to 15 minutes to attain this temperature. The
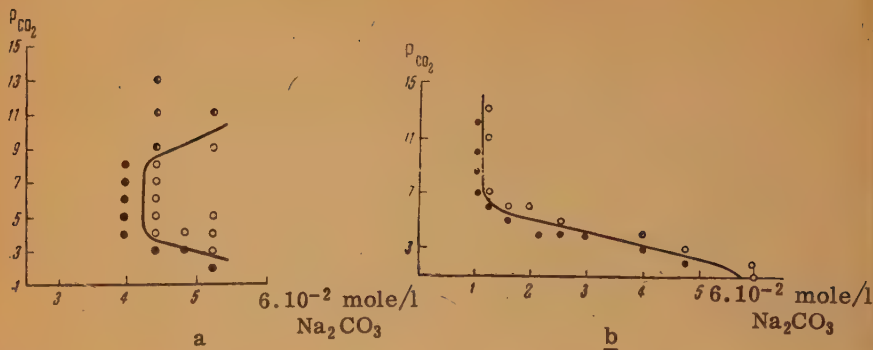
Fig. 3. Dependence of stability fields of uranyl compounds
on the concentration of Na_2CO_3 and P_{CO_2}, $t = 150°C$.

a -- $C_U = 1.5 \cdot 10^{-2}$ mole/l, b -- $C_U = 1.3 \cdot 10^{-3}$ mole/l
○ -- yellow transparent solution, ◖ -- yellow precipitate
containing CO_2, ● -- orange precipitate without CO_2

variation of temperature in the bomb during heating was not over $\pm 10°C$.
After heating, the bomb was rapidly cooled and opened. The time of cooling
did not exceed 5 minutes. The quartz container was removed from the bomb
and examined visually for the presence of the solid phase. If present, it
was rapidly removed, washed in water and analyzed for carbon dioxide.

The results of the experiments are given in Fig. 3. The curves were
drawn by interpolating between the extreme values obtained in the experi-
ments. It should be mentioned that, at room temperature, it takes several
days, and sometimes weeks, for the system to attain equilibrium. At ele-
vated temperatures, equilibrium is attained much more quickly. To find
out whether the selected heating time was sufficient for the attainment of
equilibrium, we used another method of attaining it, i.e. by changing the
carbon dioxide pressure in the system after precipitation of the solid phase.
At all points checked by this method, the precipitated uranium returned
into solution with increase in P_{CO_2}, although this reverse transition (solu-
tion of precipitate) sometimes took over 6 hours. The difference in the
time required to attain equilibrium in going from solution to the solid phase
and for the reverse process is explained by the fact that no stirring was
used in the experiments and only the surface of the precipitate was exposed
to solution. When the precipitate was incompletely dissolved it could be
seen on opening the bomb that the solution had a more intensive color di-
rectly above the precipitate than in the upper part of the bomb. It may be
considered, therefore, that the data obtained in the experiments correspond
to the state of equilibrium.

No reaction was observed between the solution and the walls of the quartz
container. More than 50 experiments were performed in the same container.

Comparison of Experimental and Computed Data

Unfortunately, it was impossible in our experiments to determine either the hydrogen ion concentration (pH) or the distribution of carbon dioxide between the liquid and gaseous phases (Σ' CO_2, P_{CO_2}). For this reason, direct comparison of the computed and the experimental data is rather difficult. If it is considered, however, that as the carbon dioxide pressure is increased the amount of carbon dioxide dissolved in the liquid phase (Σ' CO_2) increases and the pH diminishes, while increase in the concentration of Na leads to increase both in (Σ' CO_2) and pH, it is possible to compare the basic conclusions derived from the computations and experiments.

First of all, it follows from the experiments that at the temperature of 150°C, as at the standard temperature, there exists a field in the carbonate alkaline medium in which hexavalent uranium forms easily soluble compounds. The boundaries of this field for a given concentration of uranium are determined by the ratio of the concentration of sodium to the initial carbon dioxide pressure, which means a definite ratio between the concentration of dissolved carbon dioxide and the alkalinity of the solution, or ultimately, a definite concentration of free CO_3^{2-} ions. Indeed, with the same addition of soda (vertical section, Fig. 3a), the decrease in the initial CO_2 pressure leads to a decrease in the concentration of the dissolved carbon dioxide and to an increase in the alkalinity of the solution, and as a result, to the precipitation of the products of hydrolysis of uranyl ion (CO_2-free precipitate). An increase in pressure of carbon dioxide leads to an increase in Σ' CO_2 and a decrease in the pH of the solution, causing separation of a yellow precipitate which gives off carbon dioxide on being treated with HCl and is probably a uranyl monocarbonate. A decrease in the amount of added soda at constant P_{CO_2} (horizontal section, Fig. 3a) leads to the precipitation of the products of hydrolysis of the uranyl as a result of decrease in both Σ' CO_2 and pH of the solution.

It is interesting to note that, unlike the system with the initial uranium concentration of $1.5 \cdot 10^{-2}$ mole/l (Fig. 3a), the system with the initial uranium concentration of $1.3 \cdot 10^{-3}$ mole/l (Fig. 3b) did not give precipitates containing carbonate ions in the region investigated.

There is no doubt that, in a carbonate alkaline medium at t = 150°C, uranium exists in solution in the form of compounds differing from the usual complex uranyl carbonate anions. Moreover, it can be seen from the cursory analysis just presented that the main features of behavior of uranium compounds in aqueous solutions under standard conditions persist into the region of elevated temperatures up to 150°C.

Oxidation–Reduction Equilibria in a Carbonate Medium

Any hypothesis of migration of uranium in the hexavalent state must explain the reduction of at least a part of it to the quadrivalent state in which it is deposited as pitchblende. Most investigators tend to consider the S^{2-} and Fe^{2+} ions as the main reducers of uranium. The possibility of reduction of uranium precipitated as a hydroxide by these ions in a weakly alkaline, carbonate-free medium was demonstrated by the author earlier [17]. However, in a carbonate medium where the UO_2^{2+} ions are fixed in the stable uranyl carbonate complexes, it is quite natural to expect the

oxidation-reduction potential of the system to decrease.

Using thermodynamic data, Garrels [11] showed that in a carbonate-free medium the oxidation-reduction potential of the system $U^{VI} \rightleftarrows U^{IV}$ is a linear function of pH. His argument can be reduced to the following:

According to Nernst's equation, the potential of the reaction

$$UO_2^{2+} + 4H^+ + 2\bar{e} = U^{4+} + 2H_2O$$
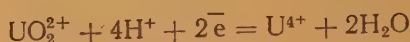
is

$$Eh = E° + \frac{RT}{nF} \log_e \frac{[UO_2^{2+}][H^+]^4}{[U^{4+}]}$$

If the solid phases of uranium hydroxide and uranium oxide are in equilibrium with the solution, the equation takes the form:

$$Eh = E° + \frac{RT}{nF} \log_e \frac{K_2 K_W^2 [H^+]^2}{K_8}.$$

Substituting the known values of the ionization constants of U^{VI} and U^{IV} in the last equation, we obtain

$$Eh = 0,482 - 0,059 \, pH.$$

In the carbonate medium, UO_2 (solid) and the complex uranyl carbonate anions attain equilibrium.

1. $[UO_2(CO_3)_3]^{4-} + 2\bar{e} = UO_2 \text{ (solid)} + 3CO_3^{2-}; \quad E_{(1)}^0 = -0,32 \text{ v};$

2. $[UO_2(CO_3)_2]^{2-} + 2\bar{e} = UO_2 \text{ (solid)} + 2CO_3^{2-}; \quad E_{(2)}^0 = -0,207 \text{ v.}$

The value of E° is easily calculated, since the values of the free energies of formation of the corresponding complex anions are known [4, 18]. The oxidation-reduction potentials of these reactions are given by the equations:

$$Eh_{(1)} = E_{(1)}^0 + \frac{RT}{nF} \log_e \frac{[UO_2(CO_3)_3^{4-}]}{[CO_3^{2-}]^3}, \qquad Eh_{(2)} = E_{(2)}^0 + \frac{RT}{nF} \log_e \frac{[UO_2(CO_3)_2^{2-}]}{[CO_3^{2-}]^2}.$$

These equations show that an increase in the concentration of the complex anion increases the oxidation-reduction potential of the equilibria, while an increase in the concentration of the CO_3^{2-} ion decreases it. The change in the oxidation-reduction potential of the equilibria as a function of

the total dissolved carbon dioxide is shown in Figs. 4 and 5.
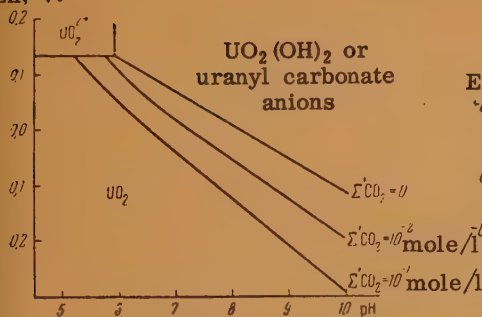
Fig. 4. Dependence of the oxida-
tion-reduction potential of the
system $U^{VI} \rightleftharpoons U^{IV}$ on pH and Σ'
CO_2 at $C_U = 10^{-3}$ mole/l,
t = 25°C.
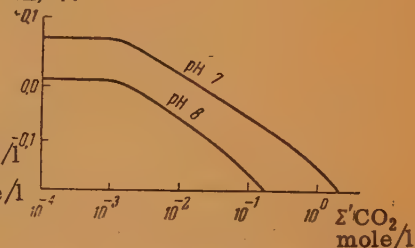
Fig. 5. Variation in the oxidation-
reduction potential of the system
$U^{VI} \rightleftharpoons U^{IV}$ as a function of Σ' CO_2
at pH = const., $C_U = 10^{-3}$ mole/l,
t = 25°C.

Discussion

On the basis of our results, it may be concluded that complex uranyl
carbonate anions actually exist under natural conditions and that the hypoth-
esis of uranium transport in hydrothermal solutions in the form of carbon-
ates meets with no objections from the physicochemical point of view. The
existence of these complexes in nature is proved by the existence of such
minerals as uranothallite -- $Ca_2[UO_2(CO_3)_3] \cdot 8-9H_2O$, andersonite --
$Na_2Ca[UO_2(CO_3)_3] \cdot 6H_2O$, swartzite -- $CaMg[UO_2(CO_3)_3] \cdot 12H_2O$,
bayleyite -- $Mg_2[UO_2(CO_3)_3] \cdot 18H_2O$, all salts of the complex tricarbonate
anion, and of voglite -- $Cu[UO_2(CO_3)_2] \cdot 10H_2O$ (from Fergana) and
$CuCa_2(CO_3)_4] \cdot 6H_2O$ (from Joachimstahl), a salt of the uranyl bi-
carbonate anion.

N. M. Nikolaeva [19] showed that in uranium-bearing natural waters
uranium is present in the form of complex uranyl carbonate anions. I. E.
Starik and L. B. Kolyadin [20] came to the conclusion that these uranium
compounds are typical in ocean waters.

The stability of the uranyl carbonate anions at elevated temperatures
suggests that this is also the form in which uranium exists in the natural
hot carbonate waters, at least up to the temperature of 150°C. It follows
from the preceding discussion that the solutions may be alkaline, neutral,
or possibly even weakly acid. The waters transporting uranium need not
be of the bicarbonate type. Addition of such salts as sodium chloride or
sulfate does not significantly affect the uranium-carbonate equilibrium.
The natural carbonate waters containing complex uranyl carbonate anions
may be of the bicarbonate, sulfate, chloride or mixed type.

The decrease in the oxidation-reduction potential of the U^{VI}--U^{IV}
equilibrium with increase in the amount of carbon dioxide dissolved in

water is of great geochemical importance. In solutions containing a suffi-
cient amount of Σ ' CO_2, hexavalent uranium may coexist with such con-
centrations of reducing agents, for example Fe^{2+} or S^{2-}, as would reduce
it in the absence of carbon dioxide; i.e., both the hexavalent uranium and
the reducing agents may be transported in the same hydrothermal solution.
Again, under certain physicochemical conditions, uranium-bearing hydro-
thermal solutions may exist unchanged in contact with rocks which under
other conditions would cause reduction of uranium.

The deposition of uranium in the form of pitchblende must be accom-
panied by the destruction of the complex uranyl carbonate anions.

On the basis of the above discussion, the accumulation of uranium in
nature is favored by the following factors.

1. Reduction of carbon dioxide pressure and consequent decrease in
the concentration of CO_2 dissolved in water. Under natural conditions CO_2
pressure may be reduced during the formation of joints when the solutions
percolating through rocks and finely jointed zones enter zones of coarser
jointing or conjugate joint systems and lose pressure as they move up-
wards. As the carbon dioxide escapes from the solution, the alkalinity of
the solution will increase and the equilibrium between the solution and the
rocks will be distrubed. In this case, the processes striving towards re-
establishment of equilibrium will be manifested in the removal of the alka-
lies and strong bases from the solution (fixation of the alkalies in the en-
closing rocks, separation of carbonates, etc.).

2. Decrease in the alkalinity of solutions leading to decrease in the
concentration of CO_3^{2-} and, therefore, to increase in UO^{2+} ions. Such
change in the alkalinity of the solution may occur by the passage of the
solutions from one rock into another. However, the diagrams show that
the pH may vary over a rather broad range in the alkaline and neutral medi-
um without substantially shifting the equilibrium. The desired effect will
occur only in acid media. Although possible, this effect is apparently very
uncommon in nature. Most intrusive, extrusive and metamorphic rocks
have neutral or weakly alkaline pore solutions (the pH of the suspensions of
these rocks is 7 and more) and only some sedimentary rocks and possibly
certain zones intensively altered by earlier hydrothermal processes can
provide sufficient acidity.

3. The precipitation of carbonate ion caused by a decrease in the con-
centration of carbon dioxide in the solution resulting from chemical reac-
tions. In nature this process may be caused by the passage of ore-bearing
solutions from one rock into another richer in such elements as Ca, Mg
and Fe, for example, from granitoids into basic rocks. In this case the
process of carbonatization of the enclosing rocks must be accompanied by
addition of carbon dioxide into the vein zone without substantial change in
the amount of Ca and Mg.

4. Decrease in the oxidation-reduction potential in connection with
change in the composition of the enclosing rocks. The flow of ore-bearing
solutions from granites into basic rocks rich in ferrous iron, into sedi-
mentary rocks rich in organic matter, into zones previously altered by
hydrothermal processes, rich in iron chlorites, iron carbonate, etc., will
lead to a diminution in the oxidation-reduction potential of the solutions.

The temperature decrease during the upward movement of the ore-
bearing solutions frequently cited in explaining ore deposition has no effect
at all. If all other conditions are stable, temperature decrease cannot
cause the destruction of the complex uranyl carbonate anions.

Thus, in the transportation of hexavalent uranium by carbonate solutions,

the conditions favorable for ore deposition can be divided into physical, determined by the tectonic development of the region and of individual structures, and chemical, determined by the composition of the country rock. It should be noted that in a given geological setting it is not always possible to ascribe the precipitation of uranium from solution to a single factor. Rather, it is a number of complexly interrelated factors that bring about the formation of ore bodies. Thus, the amount by which the pressure of CO_2 must be lowered will not be the same for solutions in contact with rocks of different composition or lying in tectonic zones which have been subjected to previous hydrothermal alterations. In this case the localization of uranium mineralization in the different areas of the deposit will be related to the tectonic movements of individual structures and to the character of the country rock.

In conclusion, it should be emphasized that the possibility of transportation of uranium by hydrothermal solutions in the form of complex uranyl carbonate anions does not at all exclude other modes of transportation, including the transportation of uranium in the quadrivalent state. Each postulated mode requires special study. The truth of the concepts presented here should be verified for each individual deposit, and the factors leading to ore deposition can be discovered only after a detailed investigation of concrete geological material and its comparison with the general relations presented above.

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THE ROLE OF FLUORINE COMPOUNDS
IN THE TRANSPORTATION OF BERYLLIUM
AND THE FORMATION OF PHENAKITE

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An analysis of the characteristic association of the principal beryllium minerals (beryl, phenakite, chrysoberyl, etc.) with the fluorine-bearing minerals (fluorite, topaz, micas, etc.) suggests that, during the endogenic process of mineral formation, beryllium may be transported in the form of complex chlorine- and fluorine- bearing compounds of the double fluoride type. It is assumed that these compounds are transported both in the gaseous phase (early stage of the process) and in the later solutions. Sublimation, i.e. separation of the element in the form of volatile compounds, is assigned an important role in the concentration of dispersed beryllium and formation of independent beryllium minerals.

A. V. Novoselova and her associates [2] studied the composition of vapors over a beryllium sodium fluoride melt (Na_2BeF_4) and showed that the molecular ratio $NaF:BeF_2$ in the vapor is near 1:1. Inasmuch as the

Turning to the experiments in the synthesis of phenakite, $Be_2[SiO_4]$, described in the literature, it should be noted that in 1949, Morgan and Hummel [3] showed that it is impossible to produce phenakite from beryllium oxide and silicon dioxide at any temperature without adding mineralizers.

The first synthetic phenakite in the form of small prismatic crystals was apparently obtained by Ebelmen (1851) by heating a mixture of BeO, SiO_2 and borax [4]. The latter was used in excess so that it is difficult to decide whether molten borax played the role of mineralizer or solvent (i. e. , crystallizator according to D. P. Grigor'ev's terminology [5]). Daubree (1854) reported that he synthesized phenakite by passing silicon tetrachloride vapor over beryllium oxide at a high temperature [6], but on repeating this experiment, H. St. Claire Deville (1861) did not find phenakite [7]. He obtained phenakite by using silicon tetrafluoride (with a trace of hydrogen fluoride) instead of silicon tetrachloride. Later (1937), A. V. Novoselova et al observed the formation of phenakite during a study of the reaction between SiF_4 and beryllium oxide [8]. Hautefeuille and Perrey (1888) heated a mixture of BeO, SiO_2, lithium vanadate and carbonate at 600-700° C for two weeks and obtained a crystalline product from which phenakite was separated after treatment with dilute hydrofluoric acid [9]. Doelter (1911) observed formation of phenakite when hydrous beryllium nitrate, silicon dioxide and ammonium fluoride (small amount to act as a mineralizer) were melted together at 1200-1300° C [10-11]. Using thermal and petrographic methods, P. P. Budnikova and A. M. Cherepanov (1950) studied the formation of phenakite from BeO and SiO_2 with addition of $2CaO \cdot SiO_2$, $2CdO \cdot SiO_2$ and MnO_2 as mineralizers (2% by weight of each). With only the first two mineralizers, phenakite did not form below 1600° C. The data of the thermal analysis show, according to the authors, that on addition of MnO_2, phenakite begins to form at 1300° C. At 1500° C, in an hour and a half, about one third of the mixture reacts (low rate of reaction) and a difficulty separable mixture of bromellite (BeO), phenakite, quartz, glass and cristobalite forms [12].

calculated partial NaF pressure in the vapor over the Na_2BeF_4 melt is higher than the vapor pressure over a melt of pure sodium fluoride (at the same temperature), it may be supposed that the gaseous phase contains complex $NaBeF_3$ molecules.

This review of the known methods of synthesis of phenakite shows that none of them, judging by the type of reactions, reproduces the conditions of formation of phenakite in nature. Neither the high temperature of most syntheses nor the presence of such crystallization media as lithium vanadate melt, etc., can be expected in the natural process.

In order to check the role of fluorine compounds in the formation of phenakite, a series of experiments were made in the synthesis of phenakite from beryllium oxide and silicon dioxide in the presence of fluorine compounds.

Experimental Section

Initial Substances

Below is a description of reagents used in the synthesis of phenakite.

a) Beryllium oxide was obtained from technical beryllium hydroxide by dissolving it in glacial acetic acid. The crystals of beryllium oxyacetate, $Be_4O(CH_3COO)_6$, separated by evaporation were recrystallized from a chloroform solution and decomposed by heating in water. After this, beryllium hydroxide was precipitated from the water solution with ammonia [13]. The washed and dried hydroxide was heated to 1100° C to constant weight and kept in a dessicator over P_2O_5. b) The silicon dioxide was obtained by hydrolysis of twice distilled silicon tetrachloride followed by drying of the silica gel on a sand bath and heating to 1100° C to constant weight. The product was 99.93% SiO_2 according to analysis. c) Beryllium fluoride $(NH_4)_2BeF_4$ synthesized by the method of Lebaux in the stream of dry carbon dioxide. d) Commercial sodium fluoride marked "analytical grade" was used as purchased. e) The lithium sodium and cesium beryllium fluorides with the composition 2:1 were kindly given to the authors by N. S. Tamm and L. M. Mikheeva.

The method of synthesis of phenakite.

The weighed samples of carefully dried oxides with the constant $BeO:SiO_2$ ratio of 2 to 1 (moles) and the catalyst were mixed in an agate mortar, transferred into quartz ampoules with thin necks and packed by light tapping. In some experiments the ampoules were sealed, but in most cases they were placed open in the furnace. Smelting furnaces were used in this work, and the temperatures were measured with standard platinum, platinum-rhodium thermocouples and maintained automatically at a given point by regulators of the ERM-47 and EPD-17 types. Temperature was raised gradually at the rate of 1-2° C per minute; the charges were cooled by turning off the furnace.

Synthesis of Phenakite with the Aid
of Mixed Mineralizers

The object of this series of experiments was to determine the effect of the addition of beryllium fluoride on some of the reactions of formation of phenakite described in the literature. These experiments were performed, therefore, with a mixture of mineralizers in which beryllium fluoride (BeF_2) was a constant component.

1. Modifying P. P. Budnikov's experiment by adding beryllium fluoride to the mixture of BeO, SiO_2 and MnO_2, we obtained in the first qualitative experiment (No. 1, Table 1) phenakite, not in the granular form but in stubby prismatic crystals 0.13 - 0.15 mm long with hexagonal prism faces and a flat rhombohedron (Fig. 1). The completeness of transformation of the oxides into the mineral is surprising considering the relatively low temperature of 800°C and the short duration of the experiment. This and
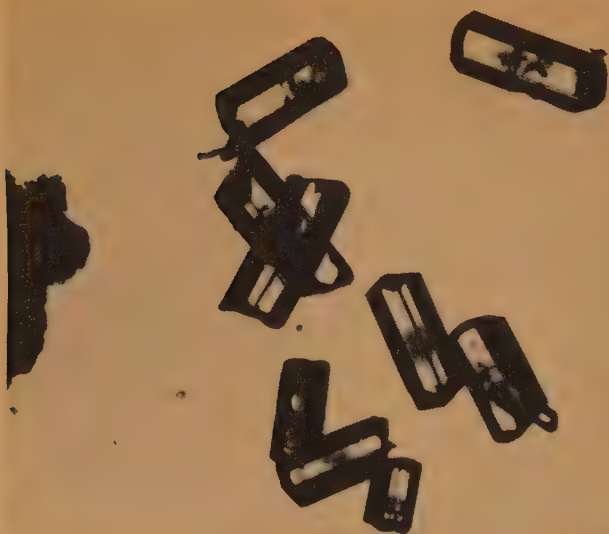
Fig. 1.   Typical form of phenakite in the reactions
(Tables 1 and 3)

the form of the mineral convincingly indicate that this is not a simple fusion of the oxides but a chemical reaction in which the mobility of beryllium and silicon is very high.   The product of reaction consisted of two phases: a) transparent crystals with refractive indices $N_g = 1.670 \pm 0.002$ and $N_m = 1.654 \pm 0.002$, which agree well with the indices for phenakite given in the literature; and b) smoky crystals of the same habit but with higher refractive indices, apparently solid solutions of tephroite in phenakite.

The powder photographs of the natural and synthetic phenakite (transparent) are identical.

Experiments Nos. 2 and 3, Table 1, show that the amount of precipitated phenakite remains practically unchanged when the addition of beryllium fluoride is increased from 10% to 50% but that when it is reduced to 1% the reaction stops.   Experiments Nos. 5, 6, and 7, Table 1, show that with the addition of beryllium fluoride (in the absence of other mineralizers) phenakite forms at the temperature of about 1200°C.   Let us recall that in the mixture of BeO, SiO_2 and MnO_2 [12], phenakite formed at the temperature above 1300°C.

In the presence of mineralizer containing MnO_2 and BeF_2, the same mixture of oxides crystallizes at 700°C !

2. In our modification of Hautefeuille and Perrey's [9] investigation of the effect of molten lithium salts on the mixture of BeO and SiO_2, we used a mixture of lithium molybdate and beryllium fluoride as a mineralizer. The reaction begins at 600–700°C, continues for several hours (two weeks in Hautefeuille and Perrey's experiment!) and phenakite is obtained in well formed crystals (in a polymineralic mass in the case of the above authors). Although the temperature in Hautefeuille and Perrey's experiment was also 600–700°C, the form of the product and the duration of the reaction indicate

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Table 1

Synthesis of Phenakite from the Oxides With Addition of Beryllium Fluoride or a Mixture of BeF_2 and MnO_2 or Li_2MoO_4

Experiment No.	Composition BeO:SiO$_2$ (moles)	Mineralizer	Temperature, °C	Duration of experiment, hours	Remarks
1	2:1	MnO_2 BeF_2	800	1	Entire mass -- crystals of phenakite, Fig. 1
2	2:1	MnO_2, 1% BeF_2, 10%	700	7	Little phenakite, rhodonite present
3	2:1	MnO_2, 1% BeF_2, 50%	700	7	Finely crystalline phenakite, 30%
4	2:1	MnO_2, 1% BeF_2, 1%	700	7	No phenakite, rhodonite present
5	2:1	BeF_2, 3%	770	6	No phenakite
6	2:1	" "	1130	6	" "
7	2:1	" 5%	1200	80	Finely crystalline phenakite, several large crystals in the sublimate
8	2:1	Li_2MoO_4, 1% BeF_2, 10%	700	7	Finely crystalline phenakite, many black spherulites
9	2:1	" "	500	5.5	No phenakite
10	2:1	" "	600	3	" "
11	2:1	Li_2MoO_4, 10% BeF_2, 1%	800	3	Phenakite, numerous black spherulites

that the action of our mineralizer differs from that of lithium vanadate and carbonate melt. Experiments Nos. 8-11, Table 1, are very similar to experiments Nos. 1-3, so far as the form of phenakite and the characteristics of the reaction are concerned.

It may be concluded from experiments 1-11, Table 1, that the double fluorides (fluoberyllates) containing Be and Mn or Be and Li are strong mineralizers. They are formed by reactions between manganese oxides or lithium molybdate and beryllium fluoride. To verify this hypothesis, a series of experiments were made.

Synthesis of Phenakite in the Presence of Fluo-beryllates of Some of the Alkali Metals

Beryllium fluoride and fluo-beryllates have considerable vapor pressure at temperatures above melting point.

Inasmuch as the data on the vapor pressure or dissociation pressure over the melts of the majority of these compounds are lacking in the literature, Table 2 presents their melting temperatures, i.e. temperatures at which their crystal lattices are destroyed.

Table 2

Melting Temperatures of Fluo-beryllates of the Composition $Me_2^+ BeF_4$, where Me^+ is Li, Na, K, Rb or Cs

Compound	Melting temperature °C	Authors
Li_2BeF_4	475	Thilo and Lehman [14]
"	461	A.V. Novoselova et al [15]
"	458	Roy, Roy and Osborn [16]
Na_2BeF_4	620	A.V. Novoselova et al [17]
"	578	Thilo [18]
K_2BeF_4	791	A.V. Novoselova et al [19]
Rb_2BeF_4	807	R.G. Grebenshchikov [20]
Cs_2BeF_4	793	A.V. Novoselova, O.N. Breusov [21]

In the series of experiments described below (Table 3) Li_2BeF_4, Na_2BeF_4 and Cs_2BeF_4 were used as mineralizers. Experiments Nos. 1-3, Table 3, show that sodium fluoride is a poor mineralizer in the mixtures of beryllium and silicon oxides. The components of NaF and BeF_2, taken separately, become active mineralizers only at temperatures over 1000°C.

Syntheses with addition of fluo-beryllates proceeded at lower temperatures and at much greater rates. In all cases, the same kind of crystalline phenakite was obtained as in experiments Nos. 1-3, 7, 8 and 11 of Table 1, but unlike the phenakite synthesized in those experiments, it was not contaminated with manganese or molybdenum oxide.

Comparison of the temperatures of the beginning of reactions* in experiments No. 6, Table 3, and Nos. 8 and 10, Table 1, shows clearly that they are similar. Evidently, as has already been mentioned, when both Li_2MoO_4 and BeF_2 are present, they react to form a fluo-beryllate which serves as a catalyst in the reaction of formation of Phenakite. Therefore, the temperature of the beginning of reaction when Li_2BeF_4 is added is practically the same as with the mineralizer composed of Li_2MoO_4 and BeF_2.

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*It was not possible to measure this temperature thermographically, because of the relatively low heat and velocity of these reactions.

Comparison of the melting temperature of fluo-beryllates (Table 2) with the corresponding temperatures of the beginning of reactions (Nos. 6, 11, 13, Table 3) shows that the latter are from 150°C to 300°C higher than the melting temperatures of the fluo-beryllates.

Table 3

Synthesis of Phenakite from the Oxides With the Addition of Sodium Fluoride and Fluo-beryllates of Lithium, Sodium and Cesium $(Me_2^+ BeF_4)$

Experiment No.	Composition $BeO:SiO_2$ (moles)	Mineralizer wt. %	Temperature, °C	Duration of experiment, hours	Remarks
1	2:1	NaF, 8%	800	4.5	No phenakite
2	2:1	" 1.3%	1000	1.3	" "
3	2:1	" 8%	1050	3	Individual phenakite crystals in sublimate at the neck of the ampoule
4	2:1	Li_2BeF_4, 2%	400	7	No phenakite
5	2:1	" "	500	3	" "
6	2:1	" "	650	9	Finely crystalline phenakite
7	BeO (without SiO_2)	" "	800	3.5	Phenakite crystals throughout the mass of BeO
8	2:1	Na_2BeF_4, 6%	600	3	No phenakite
9	2:1	" "	700	7	" "
10	2:1	" "	800	4.5	" "
11	2:1	" "	900	5	The entire mass -- coarsely crystalline phenakite
12	2:1	" "	1100	0.5	The entire mass -- coarsely crystalline phenakite
13	2:1	Cs_2BeF_4 5%	1020	3.5	Individual equidimensional phenakite crystals

Since a prolonged heating at a temperature intermediate between the melting temperature of a fluo-beryllate and the temperature of the beginning of

reaction (experiments Nos. 9 and 10, Table 3) does not result in the formation of phenakite, it is clear that the fluo-beryllate melt is not a catalyst in the reaction. To start the [reaction of] formation of phenakite, it is necessary that the reacting substances have a certain definite vapor pressure and possibly a definite molecular form.

It was found that during the formation of phenakite a gaseous phase is present in the reaction vessel which is rather easily hydrolyzed by blowing air containing water vapor into the vessel. The results of experiments conducted in vacuum show that this gaseous phase is the mobile medium from which phenakite crystals are formed. Evidently, during the breakdown of the volatile beryllium complexes and the withdrawal of beryllium into the crystal lattice of the growing Be_2SiO_4 the remaining products react again with the beryllium oxide and make it mobile. It is difficult to explain in any other way the effect of such small additions of fluo-beryllates (it should be noted that of the 2-6% of the mineralizers added, the larger part reacted with the walls of the ampoule).

It should be noted that beryllium migrates readily in the gaseous phase, for in most of the experiments phenakite crystals were found on the ampoule walls as far as 5 cm from the mixture of oxides. The source of silica for these crystals was not clear. In order to find out how silica behaves in this reaction, experiment No. 7, Table 3, was performed.

a   b
before   after
reaction   reaction
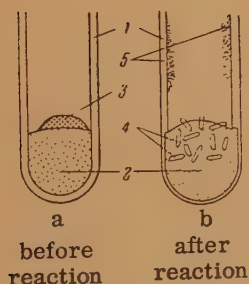
Fig. 2. Diagram of experiment
No. 7 (Table 3)

1 -- quartz ampoule, 2 -- beryllium oxide, 3 -- Li_2BeF_4, 4 -- phenakite crystals, 5 -- coating of fibrous SiO_2
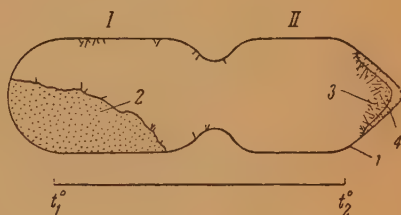
Fig. 3. Diagram of experiment
in "distillation" of phenakite.

1 -- quartz ampoule, 2 -- mixture of BeO:SiO_2 = 2:1 with 2% Na_2BeF_4, 3 -- large phenakite crystals, 4 -- finely crystalline phenakite

Beryllium oxide was poured into a quartz ampoule (Fig. 2 a) and covered without mixing with lithium fluo-beryllate. The ampoule was heated for 3½ hours at 800°C, and it was found that coarsely crystalline phenakite (3-4 mm), evenly distributed through the ampoule, formed in the beryllium oxide (Fig. 2 b). The ampoule walls were corroded to the depth of 1.0 mm,

the silica from the walls contributing to the making of phenakite. More-
over, nearer the neck of the ampoule there developed a hair-like coating
composed, according to analysis, of 99.0% SiO_2. The microscope re-
vealed isotropic fibers, and it was possible to determine one refractive
index, $N' = 1.452 \pm 0.003$. This shows that silica in this reaction also
passes through the gaseous phase in the form of volatile compounds of
some kind.

But if both Be and Si pass through the volatile phase, could not phena-
kite be "distilled" by creating a temperature gradient in the reaction vessel?

To test this idea, a mixture of oxides and mineralizer was placed in
chamber I of a quartz ampoule constricted in the middle, the ampoule was
sealed in vacuum and placed in the furnace so that the empty chamber II
was at a lower temperature. After the reaction was complete, relatively
large phenakite crystals (up to 5-6 mm long) were found grown on a dense
crust of finely-crystalline phenakite (Fig. 4). The size of the crystals in-
creased with temperature and duration of the experiment (compare Figs.
4 and 5). However, at the temperature above 1300°C the crystals became
corroded and rounded. These experiments show that under favorable condi-
tions it is possible, theoretically at least, to grow large phenakite crystals.*
In this "distillation" it was possible, as shown by spectrographic analysis,
to get rid of the traces of such elements as Na and Al. "Distilled" phena-
kite was spectrographically free of sodium introduced into the reaction in
the form of Na_2BeF_4 (phenakite crystals from chamber I of the ampoule
contained traces of Na and Al).

It is interesting to note that in chamber II, two types of phenakite crys-
tals are sometimes found--long prismatic (a hexagonal prism modified by
a flat rhombohedron) and equidimensional (rhombohedral). The relation
between these crystals is shown in Fig. 6. The equigranular crystals are
evidently earlier. Similar relations are observed in nature, the late
phenakite always forming prisms (Fig. 7). As the temperature rises to
1100-1200°C, a second hexagonal prism appears on the prismatic crystals.

A comparison of experiments with different mineralizers (Nos. 6, 11,
13, Table 3) and the data of Table 2 show that the temperature of formation
of phenakite increases with the increase in the melting temperature of the
corresponding fluo-beryllate from Li_2BeF_4 to Na_2BeF_4 and $CsBeF_4$.

In all cases the crystal habit of phenakite is essentially independent of
the alkali metal cation. A similar phenomenon was observed in the experi-
ments with mixed mineralizers. It must be supposed that the mechanism
of all these reactions is similar.

Discussion of Results

The present work provides an experimental confirmation of the hypoth-
esis formulated earlier in geochemical literature to the effect that beryl-
lium may be extracted from an inert solid phase in the presence of fluorine
compounds and transformed into a gaseous phase. Moreover, in the

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*The synthesis of phenakite with the addition of fluo-beryllates may be rec-
ommended for obtaining this mineral in large amounts and in sufficiently
pure form. If sodium fluo-beryllate is used, it is best to let the reaction
proceed at 1000-1100°C, for then it is completed in only a few hours.

Fig. 4. "Distilled" phenakite
(900°C, 3 hours) x 10
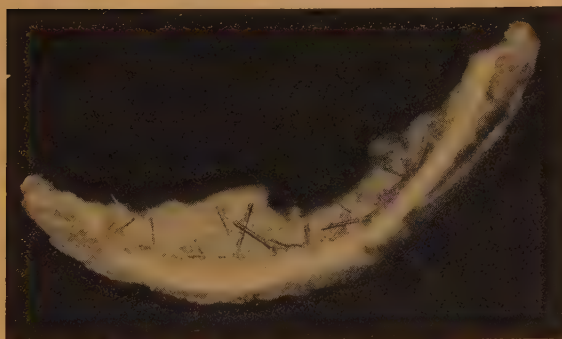
Fig. 5. "Distilled" phenakite
(1100°C, 4 hours) x3
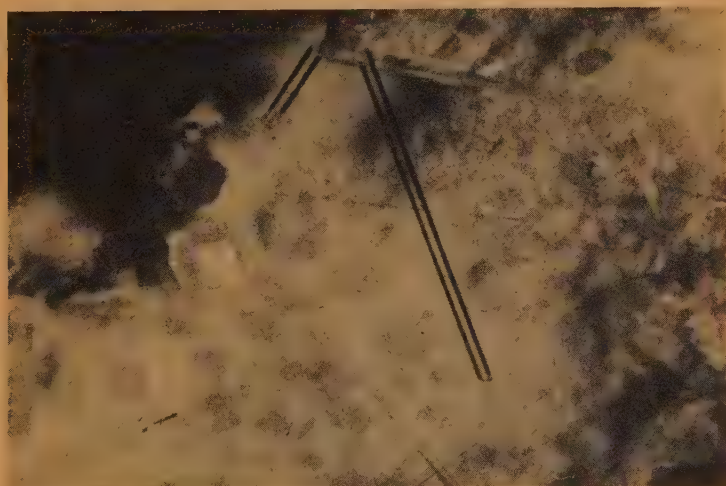
Fig. 6. Rhombohedral and prismatic forms of phenakite x20

Fig. 7.   Crystals of natural phenakite on corroded
microcline from a pegmatite (N.E. Zalashkova's
collection) x4

presence of an excess of cations of alkali metals characteristic of natural
conditions, beryllium may be transported in the gaseous phase in the form
of fluo-beryllates.

In the presence of silica and fluo-beryllates in the system, silica passes
into the gaseous phase and phenakite crystallizes from it.   The outward
aspects of the reaction leading to the synthesis of phenakite place it among
the so-called "transport" reactions studied by Schaffer, Jacob, Etzel, and
Morcher [22, 23, 24] and others.   In their experiments the transfer of
silicon was achieved through the formation of compounds in which silicon
is bivalent.   The transfer of Fe_2O_3 and Cu_2O was achieved through the
formation of volatile halide compounds later hydrolyzed by water vapor.

In our case the first process is impossible because of the absence of any reducing agents. Special experiments show that careful removal of traces of water from the reacting mixture had no noticeable effect on the rate of reaction. Evidently we are dealing here with a third variety of reaction of this type. The transfer of oxygen in this reaction is explained apparently by the formation of silicon oxyfluorides. Possibly the following reactions occur:

$$SiO_2 + 2NaBeF_3 \rightleftarrows SiF_4 + 2BeO + 2NaF \qquad (1)$$
$$SiF_4 + BeO \rightleftarrows SiOF_2 + BeF_2 \qquad (2)$$
$$4SiOF_2 + 2NaBeF_3 \rightleftarrows Be_2SiO_4 + 3SiF_4 + 2NaF \qquad (3)$$
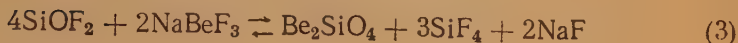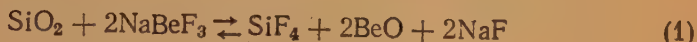
In these equations $SiOF_2$ is taken for the sake of simplicity, but actually more complex polymers, fluosiloxanes are formed from these reactions, as, for example, from the reaction between SiF_5 and metallic oxides [25] at high temperatures. These compounds are unstable and are easily decomposed and hydrolyzed.

Summary

1. The conditions of formation of phenakite from beryllium oxides, silica and fluo-beryllates have been determined.

2. It has been established that phenakite forms from BeO and SiO_2 in the presence of fluo-beryllates, as a result of heterogeneous reactions, with the participation of the gaseous phase.

3. Because of the occurrence of "transport" reactions, phenakite may be "distilled" in the presence of fluo-beryllates. The probable mechanism of transfer of Be, Si and O during a "transport" reaction is suggested.

4. The characteristics of the paragenesis of phenakite in different types of deposits and the morphological similarity of the crystals of synthetic and natural phenakite suggest that fluo-beryllates play a leading role in the process of formation of endogenic phenakite.

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MIGRATION OF COMPONENTS
DURING THE FORMATION OF SKARNS
AT THE TASHBULAK DEPOSIT

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During the period 1953-1956, the author was engaged in detailed pros-
cting and mapping in the region lying to the west of the well-known Altyn-
opkan mineralized area in the Kuraminskii Range.

During this work, which led to a detailed exploration of the Tashbulak
olymetallic deposit, the author made a study of the relationship between
olymetallic mineralization in skaran and in different igneous rocks
idely distributed throughout the area. Particular attention was paid to
e problem of introduction and removal of different components dur-
g the process of skarn and ore formation relative to the composition of
fferent igneous rocks.

The Tashbulak deposit is located in the Matchinskii region of the Lenin-
id district in the Tadzhik SSR. This area is in the foothills of the north-
estern end of the Karamazar-Kuraminskii Range, one of a system of
outhwestern ranges of Northern Tien Shan. The Tashbulak deposit is also
e westernmost part of a continuous mineralized zone including the
rdob, Tashgeze, Altyn-Topkan, Chalata and Myshik-Kol deposits lying
the so-called Altyn-Topak limestone ridge. The ridge is the northern
mb of the Kuraminskii anticlinorium formed during an early stage of
ariscan orogeny and containing a granodiorite batholith in its core. At
e base of the section of the northern limb lies a Silurian sequence com-
osed of metamorphosed volcanics and shales. It is overlain [in] angular
nconformity by [the] Middle and Upper Devonian and Lower Carboniferous
mestones. The eroded surface of the limestones is covered by Upper
aleozoic extrusives. All these strata are cut by a system of dikes and
ke-like and stock-like intrusives of different composition, referred to as
e Upper Paleozoic "minor intrusions."

The approximate age sequence (from older to younger) of the minor
trusives, established by the author for this region, is as follows:
roxene lamprophyres,* granodiorite porphyries, granite porphyries,

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This is the first find of these rocks in the Karamazar region. They dif-
r from common spessartites in having pyroxene as the only dark mineral.

quartz porphyries, spessartites and kersantites, granophyres, alaskite
porphyries and microgranophyres, and earlier and later diabases.

Field and laboratory investigations revealed a number of regularities in
the formation of skarns and ores which had not been recorded before from
the Altyn-Topkan mineralized area.

1) Polymetallic mineralization is localized in skarns formed, not only
at the contact between limestones and granodiorite porphyries, as stated
by Abdullaev (1957), but at the contact between limestones and pyrox-
ene lamprophyres, which are older than the granodiorite porphyries.
Mineralization also occurs in skarns formed at the contact of limestones
with much younger kersantites, spessartites and diabases. As a
rule, the width of the outer contact zones, carrying economic poly-
metallic deposits, is greater than of the inner contact zones, which
contain only traces of mineralization.

2) The chemical and mineralogical composition and structure of the
outer contact zones are exceptionally uniform and do not depend on the
character of the igneous rocks at the contact. The mineralogical and
chemical composition of the endoskarns, on the other hand, is directly
dependent on the type of parent igneous rock.

The metasomatic changes in the different igneous rocks and in the con-
tact limestones include:

In granodiorite porphyries: development of pyroxene and garnet,
epidotization, chloritization, silicification and carbonatization.

In lamprophyres: a) In spessartites--development of actinolite
and sometimes potash feldspar, epidotization, albitization, chloritiza-
tion, silicification and carbonatization. Moreover, common hornblende
is commonly replaced by pyroxene. b) In pyroxene lamprophyres--
uralitization of the pyroxene, epidotization, chloritization, silicifica-
tion, and carbonatization.

In diabases: epidotization, albitization, chloritization, silicifica-
tion and carbonatization.

In limestones: formation of pyroxene and garnet, epidotization,
chloritization and carbonatization. Infrequently pyroxene is associated
with wollastonite.

To determine the role of the intruded rock in the formation of skarn and
the balance between introduction and removal of different components, the
author made a comprehensive study of the four most representative sec-
tions. The sections were taken through the contacts of the limestones with
granodiorite porphyries, pyroxene lamprophyres, diabases, and spessar-
tites. Several samples were collected at varying intervals in each section
from the exo- and endo-skarns of weakly metamorphosed and strongly
metamorphosed limestones (skarn minerals up to 30% and over 50% re-
spectively.) Samples were also collected from unmetamorphosed lime-
stones and igneous rocks. The extremely sharp contacts between
the endo- and exo skarns should be mentioned; the former preserve the
relict porphyritic texture of igneous rocks; the latter inherit the bedding of
limestones.

After examination of thin sections and refinement of the intervals
marked in the field, complete analyses were made of representative
specimens of exo skarns, endo skarns, igneous rocks and unmetamorphosed
limestones, and their specific gravities were determined.

A comparison of chemical analyses and microscopic data showed that in
the four sections there were practically no limestones, granodiorite por-
phyries or pyroxene lamprophyres untouched by postmagmatic processes.

r this reason the author's analyses of granodiorite porphyry (specimen
and pyroxene lamprophyre (specimen 169) were substituted by the
raged results of six and two analyses, respectively, which had been
de on fresh samples of these rocks.

The limestones were analyzed by the author by thermogravimetry and
ir insoluble residues were also determined. The analyses of 33 speci-
ns showed that, on an average, the 800-meter section of the D_3-C_1
estones contains 5-6% of insoluble residue composed mainly of clay
erals, 8-10% of dolomite and 80-85% of calcite. Additional chemical
lyses of 12 specimens of limestone from the neighboring (Chalatinskii)
tion showed that only one specimen contained 26.36% SiO_2 and 4.41%
O_3, while in the other specimens the content of silica and alumina aver-
d for the 1000-meter thickness of limestone 3.48% and 0.95%,
pectively.

In view of these facts, it was considered permissible to take the chemi-
analysis of limestone specimen 18171 as representative for all four
tions.

The results of analyses are given in Tables 1, 2, 3 and 4 according to
tions.

For each analysis there are two vertical columns of figures in the
les. One column shows the percentage of the oxides; the other, their
tent in grams per 100 cm^3.

Columns 10 and 11 record differences in mineral content in pure
estones and exo skarns; columns 12 and 13 present the same
erences for unaltered igneous rocks and endo-skarns. Columns 14
15 present the remainder of the constituents participating in the
mation of 200 cm^3 of exo- and endo skarns.

In addition to the tables, diagrams were drawn showing the additions
subtractions of the main skarn-forming [constituents]. The horizontal
e in each diagram represents the composition of unmetamorphosed lime-
nes and igneous rocks corresponding to the specimens at the end of each
tion (18171, 37*, 169, 19, 164). Below and above this line lie [the] re-
ns of alteration of [the] rock types, i.e., the regions of endoskarns
ght) and exoskarns (left). The region below the horizontal line repre-
ts removal of components; the region above it, addition of components.
For example, Table 1 shows that 100 cm^3 of pure limestone (specimen
71) contain 11.75 g SiO_2 (column 3) while the same volume of exoskarn
ecimen 35, column 5) formed from this limestone contains 136.48 g
$_2$.

In 100 cm^3 of granodiorite porphyry there are 158.26 g SiO_2 (column 9),
le the same volume of endoskarn formed from it contains 152 g SiO_2
ecimen 36, column 7). It follows from these data that to convert 100
^{3} of limestone into exoskarn, 124.47 g SiO_2 must be added to the 11.75
iO_2 already present in the limestone (column 10). Of this amount,
nodiorite contributes 6.15 g SiO_2, left after formation of the endoskarn;
the larger part, 118.58 g, is brought in by solutions (column 14).

In Fig. 1 (see diagrams facing page) the behavior of silica is repre-
ted by a double line. The line shows the behavior of silica at the con-
t between two reacting nonequilibrium media, carbonate (limestone,
cimen 18171) and aluminosilicate (granodiorite porphyry) even more

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The results of chemical analyses of specimens 37 and 169 were substituted
verage values calculated from 6 and 2 analyses respectively.

Table 1

Chemical Composition of Skarns and Parent Rocks and Addition and Subtraction of Components During the Formation of Skarns (section through contact between limestones and granodiorite porphyry in trench No. 95)

Components	Sp. 18171 limestone		Sp. 35, garnet-pyroxene exoskarn		Sp. 36, garnet-epidote endoskarn		Granodiorite porphyry[a]		Difference between data of columns 3 and 5, g/100 cm³		Difference between data of columns 7 and 9, g/100 cm³		Average balance of components for the zone	
	wt. %	g/100 cm³	wt. %	g/100 cm³	wt. %	g/100 cm³	wt. %	g/100 cm³	+	−	+	−	+	−
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	4,40	11,75	40,74	136,48	46,66	152,11	63,56	158,26	124,73			6,15	118,58	
TiO_2	0,05	0,13	0,53	1,77	0,65	2,12	0,87	0,94	1,64		1,18		2,82	
Al_2O_3	1,68	4,48	12,02	40,26	14,89	48,54	13,96	34,76	35,78		13,78		49,56	
Fe_2O_3	0,35	0,93	4,82	16,14	5,91	19,30	0,82	2,04	15,21		17,26		32,47	
FeO	0,39	1,04	1,15	3,85	1,70	5,53	2,41	6,00	2,81			0,47	1,34	
MgO	3,60	9,61	4,25	14,24	3,15	10,20	1,85	4,60	4,63		5,60		10,23	
MnO	0,11	0,29	1,90	6,56	0,78	2,52	0,08	0,20	6,07		2,32		8,39	
CaO	48,79	130,27	29,75	99,66	20,44	66,53	5,23	13,02		30,61	53,51		22,90	
Na_2O	0,08	0,21	0,30	1,00	0,43	1,40	2,37	5,90	0,79			4,50		3,71
K_2O	0,39	1,04	0,04	0,13	1,12	3,62	4,66	11,60		0,91		7,98		8,89
CO_2	39,38	105,14	3,20	10,72	2,16	7,06	3,16	7,84		94,42		0,78		95,20
H_2O	0,12	0,32	0,24	1,14	0,20	0,65	0,17	0,42	0,82		0,23		1,05	
P_2O_5	0,04	0,11	0,10	0,33	0,16	0,54	0,17	0,42	0,22		0,12		0,34	
Pb	0,08	0,21	0,12	0,40	0,12	0,39	0,08	0,19	0,19		0,20		0,39	
Zn	0,05	0,13	0,08	0,27	0,06	0,19	0,05	0,12	0,14		0,07		0,21	
Cl	0,01	0,03	0,01	0,03	0,01	0,03	0,01	0,02			0,01		0,01	
$S+SO_3$	0,01	0,03	0,05	0,16	0,07	0,23	0,01	0,02	0,43		0,31		0,34	
rem.	0,14	0,37	1,00	3,35	1,64	5,34	0,84	2,09	2,98		3,25		6,23	
Total	99,67	266,19	100,40	336,59	100,15	321,30	99,80	248,47	196,14	125,94	97,74	19,88	254,86	107,80
Sp. g.	2,67		3,35		3,26		2,49							

[a] Average of six analyses

Note: Comma represents decimal point.

Table 2

Chemical Composition of Skarns and Parent Rocks and Addition and Subtraction of Components During the Formation of Skarns (section through contact between limestones and pyroxene lamprophyres, trench No. 31)

Components	Sp. 18171 limestone		Sp. 167, garnet-pyroxene exoskarn		Sp. 168, epidote-uralite endoskarn		Pyroxene lamprophyre[a]		Difference between data of columns 3 and 5, g/100 cm³		Difference between data of columns 7 and 9, g/100 cm³		Average balance of components for the zone	
	wt. %	g/100 cm³	wt. %	g/100 cm³	wt. %	g/100 cm³	wt. %	g/100 cm³	+	-	+	-	+	-
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	4,40	11,62	42,74	128,90	35,00	105,00	49,80	147,00	117,28			42,0	75,28	
TiO_2	0,05	0,13	0,55	1,66	0,60	1,80	1,42	4,23	1,53			2,43		0,90
Al_2O_3	1,68	7,15	10,32	39,70	10,93	32,75	15,32	46,50	32,55			13,75	18,80	
Fe_2O_3	0,35	0,93	3,00	9,06	5,22	15,66	3,41	10,08	8,13		5,58		13,71	
FeO	0,39	1,04	2,70	8,15	2,23	6,69	6,32	10,87	7,11			4,18	2,93	
MgO	3,60	9,61	7,30	22,20	5,10	15,30	5,51	10,64	12,59		4,66		17,25	
MnO	0,11	2,94	2,24	6,78	2,20	6,60	0,19	0,56	3,84		6,04		9,88	
CaO	48,79	130,20	23,00	69,40	23,07	69,21	7,30	21,67		60,80	47,54			13,26
Na_2O	0,08	0,21	0,26	0,78	0,87	2,63	3,75	11,83	0,57			9,20		8,63
K_2O	0,39	1,04	0,87	2,65	0,21	0,63	1,46	4,36	1,61			3,73		2,12
CO_2	39,38	105,00	4,70	15,90	10,80	32,40	3,90	11,54		89,10	20,86			68,24
H_2O	0,12	0,32	0,28	0,84	0,18	0,54	0,82	2,46	0,52			1,92		1,40
P_2O_5	0,04	0,11	0,13	0,39	0,27	0,81	0,56	1,66	0,28			0,85		0,57
Pb	0,08	0,21	0,04	0,12	0,07	0,21	0,08	0,19		0,09	0,03		0,23	
Zn	0,05	0,13	0,10	0,30	0,06	0,18	0,05	0,12	0,17		0,06		0,16	
Cl	0,01	0,03	0,03	0,09	0,05	0,05	0,01	0,02	0,03		0,13		0,88	
S	0,01	0,03	0,04	0,12	0,27	0,81	0,04	0,02	0,09		0,79			0,06
rem.	0,14	0,37	1,52	4,58	3,40	10,20	0,40	1,18	4,21		9,02		13,23	
Total	99,67	266,19	99,82	302	100,53	300	100,00	297	190,51	149,99	94,71	78,06	152,35	95,18
Sp. g.	2,67		3		3,00		2,97							

[a] Average of two analyses

Note: Comma represents decimal point.

Table 3

Chemical Composition of Skarns and Parent Rocks and Addition and Subtraction of Components During the Formation of Skarns
(section through contact between limestones and diabases, trench No. 98)

Components	Sp. 18171 limestone		Sp. 17, pyroxene-garnet exoskarn		Sp. 18, chlorite-epidote endoskarn		Sp. 19 diabase		Difference between data of columns 3 and 5, g/100 cm³		Difference between data of columns 7 and 9, g/100 cm³		Average balance of components for the zone	
	wt. %	g/100 cm³	wt. %	g/100 cm³	wt. %	g/100 cm³	wt. %	g/100 cm³	+	-	+	-	+	-
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	4,40	11,75	39,20	117,99	49,66	147,49	51,36	143,29	106,24		4,20		102,04	
TiO_2	0,05	0,13	0,35	1,05	0,62	1,84	0,75	2,95	0,92			1,11		0,19
Al_2O_3	1,68	4,48	7,79	23,44	15,87	47,15	17,28	48,21	18,96			1,06	17,90	
Fe_2O_3	0,35	0,93	7,67	23,08	3,54	10,48	3,00	8,77	22,15		1,71		23,86	
FeO	0,39	1,04	0,30	0,90	3,30	9,79	4,15	11,55		0,44		1,76		1,90
MgO	3,60	9,61	5,50	17,76	5,66	16,78	5,26	14,64	8,15		2,14		10,29	
MnO	0,11	0,29	2,60	7,82	0,56	1,66	0,26	0,74	7,53		0,92		8,45	
CaO	48,79	130,77	26,60	80,06	11,36	33,52	7,48	20,82		50,21	12,70			37,51
Na_2O	0,08	0,21	0,25	0,75	1,36	4,04	0,58	1,02	0,54		2,42		2,96	
K_2O	0,39	1,04	0,06	0,02	3,46	10,22	4,66	12,94		1,02		2,72		3,74
CO_2	39,38	105,14	6,40	19,26	1,30	3,85	1,00	2,79		85,88	1,06			84,82
H_2O	0,12	0,32	0,34	1,93	0,26	0,77	0,10	0,28	1,61		0,49		2,10	
P_2O_5	0,04	0,11	0,22	0,66	0,06	0,18	0,37	1,04	0,55			0,86		0,31
Pb	0,08	0,21	0,44	1,32	0,05	0,15	0,09	0,25	1,11			0,10	1,01	
Zn	0,05	0,13	1,09	3,28	0,09	0,27	0,09	0,25	3,15		0,02		3,17	
Cl	0,01	0,03			0,01	0,03	0,01	0,03		0,03		0,19		0,03
$S+SO_3$	0,01	0,03	0,14	0,42	0,05	0,15	0,12	0,34	0,39		0,38		0,20	
rem.	0,14	0,37	2,00	6,02	2,76	8,18	2,80	7,80	5,65				6,03	
Total	99,67	266,19	100,35	305,76	99,97	296,55	99,36	278,31	176,95	137,28	26,04	7,80	178,01	128,50
Sp. g.	2,67		3,05		2,97		2,79							

Note: Comma represents decimal point.

Table 4

Chemical Composition of Skarns and Parent Rocks and Addition and Subtraction of Components During the Formation of Skarns (section through contact between limestones and spessartite, trench No. 29)

Components	Sp. 18171 limestone		Sp. 215, garnet-pyroxene exoskarn		Sp. 162, chlorite-epidote endoskarn		Sp. 164, spessartite		Difference between data of columns 3 and 5, g/100 cm³		Difference between data of columns 7 and 8, g/100 cm³		Average balance of components for the zone	
	wt. %	g/100 cm³	wt. %	g/100 cm³	wt. %	g/100 cm³	wt. %	g/100 cm³	+	−	+	−	+	−
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	4,40	11,62	36,70	97,70	46,56	134,50	51,70	137,30	86,08			2,80	83,20	
TiO_2	0,05	0,13	0,55	1,45	0,65	1,87	0,80	2,13	1,32			0,26	1,06	
Al_2O_3	1,68	7,15	7,32	19,47	18,11	52,20	15,37	40,80	12,32		11,40		23,72	
Fe_2O_3	0,35	0,93	2,48	6,60	5,75	16,51	3,13	8,33	5,67		8,28		13,95	
FeO	0,39	1,04	2,00	5,33	2,00	5,76	3,40	9,05	4,30			3,29	1,01	
MgO	3,60	9,61	8,70	23,30	1,80	5,19	4,30	11,40	13,70			6,21	7,49	
MnO	0,11	2,94	1,46	3,88	0,66	1,90	0,40	1,06	0,94		0,84		1,78	
CaO	48,79	130,20	25,45	67,70	13,75	39,63	7,60	20,20		62,50	19,43			43,07
Na_2O	0,08	0,21	0,40	1,06	4,10	11,80	2,10	5,58	0,85		6,22		7,07	
K_2O	0,39	1,04	0,05	0,13	0,95	2,74	4,44	11,80		0,91	1,83			9,07
CO_2	39,38	105,00	11,10	29,55	3,60	10,35	3,20	8,52		75,45		9,06		73,62
H_2O	0,12	0,32	0,24	0,64	0,14	0,40	0,36	0,96	0,32		0,40			0,24
P_2O_5	0,04	0,11	0,18	0,48	0,49	1,41	0,38	1,01	0,37			0,56	0,77	
Pb	0,08	0,21	0,02	0,05	0,01	0,03	0,07	0,18		0,16		0,15		0,31
Zn	0,05	0,13	0,10	0,27	0,04	0,11	0,08	0,21	0,14			0,10	0,04	
Cl	0,01	0,03	0,02	0,05	0,03	0,09	0,02	0,05	0,02		0,04		0,06	
SO_3	0,01	0,03	0,15	0,04	0,20	0,57	0,08	0,24	0,01		0,36		0,37	
rem.	0,14	0,37	3,70	9,84	1,40	4,00	2,50	6,65	9,47			2,65	6,82	
Total	99,67	266,19	100,54	267,54	100,27	289,06	99,93	264,44	135,51	139,02	48,80	25,08	147,34	127,21
Sp. g.	2,67		2,66		2,88		2,66							

Note: Comma represents decimal point.

clearly than the table. In the segment A - B which represents the garnet
pyroxene exoskarn zone, 124.7 g of SiO_2 were added per 100 cm^3 of pure
limestone, while the right side of the diagram shows that silica was sub-
tracted from granodiorite porphyry.

The final balance of a component is obtained by subtracting positive and
negative vertical segments.

The behavior of the other oxides is also easily traced on this diagram:

1. The entire amount of the oxides of aluminum, magnesium, ferric
iron and manganese participating in the formation of skarn was introduced.

2. The content of ferrous iron was diminished in the granodiorite por-
phyry and, together with introduced ferrous iron, went into the formation
of exoskarn.

3. Calcium was partially removed from the limestone and, together
with added calcium, formed endoskarn.

Thus, Fig. 1 and Table 1 show that, in the process of metamorphism
of 100 cm^3 of limestone and 100 cm^3 of granodiorite porphyry, the post-
magmatic solutions introduced the following amounts of oxides (in grams)
into the skarns:

$$SiO_2 = 118,58 \qquad FeO = 1,34$$
$$Al_2O_3 = 49,56 \qquad MgO = 10,23$$
$$Fe_2O_3 = 32,47 \qquad MnO = 8,39$$
$$CaO = 22,9$$

The removal of components amounted to 95.20 g CO_2 and 3.71 g Na_2O. On
the whole, addition predominated over removal.

An examination of figures and tables and a comparison of the behavior
of the main components during the formation of skarns in all four sections
show that:

1. Silica is an introduced constituent in the overwhelming majority
of cases. It goes into the [formation] of exoskarns, [because] its content
in endoskarns is almost the same as in the igneous rocks.

2. Alumina behaves rather uniformly; it goes mainly into the formation
of exoskarns, being largely contributed by solutions and, to a less extent,
by the igneous rocks (Figs. 2 and 3). Aluminum is also added to the
endoskarns formed from granodiorite porphyry spessartite.

3. Lime is contributed by the limestone and goes into the making of
endoskarns.

4. Carbon dioxide is removed.

5. Ferric oxide is an entirely introduced oxide and goes into the genera-
tion of both endo- and exoskarns.

6. Ferrous oxide is removed from the igneous rocks and, together with
ferrous oxide brought in by solutions, contributes to the formation of
exoskarns.

7. Manganese oxide is contributed entirely by postmagmatic solu-
tions.

8. A certain regularity is observed in the configuration of the right and
left parts of the diagrams when all four sections are examined. Namely,
on the right side of each diagram, which represents the transformation of
igneous rocks into endoskarn, the average vertical span of the curves is
much smaller than on the left side. This indicates that addition and sub-
traction of components played a relatively unimportant role in the forma-
tion of endoskarn and that the process consisted mainly in the transforma-
tion of the primary rock-forming minerals into postmagmatic minerals of
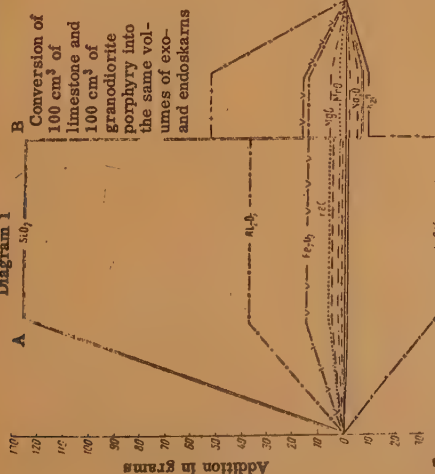
Addition and Subtraction of Components During the Formation of Skarns
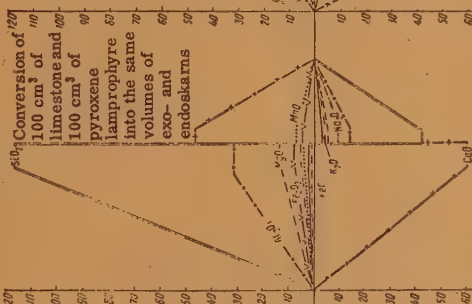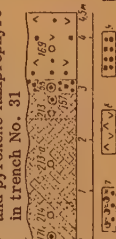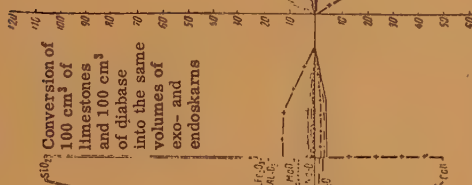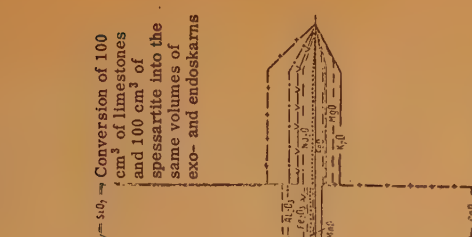
1. limestone, 2. slightly metamorphosed limestone, 3. metamorphosed limestone, 4. garnet-pyroxene exoskarn, 5. pyroxene-garnet exoskarn, 6. granodiorite porphyry, 7. garnet-epidote endoskarn, 8. pyroxene lamprophyre, 9. epidote-uralite endoskarn, 10. diabase, 11. spessartite, 12. chlorite-epidote endoskarn, 13. epidotization, 14. uralitization, 15. chloritization, 16. samples for thin sections, 17. samples for silicate analysis.

similar composition. This is fully confirmed by the following petrographic data:

In granodiorite porphyries feldspar (andesine) and some of the dark minerals are replaced by pyroxene, garnet, epidote and chlorite. In this process the amount of silica decreased slightly and the amount of alumina and ferric oxide, and especially lime, increased. Typically, the soda and potash of the feldspars of the grandodiorite porphyry were almost completely removed and did not participate in the postmagmatic transforma-tions of the parent rock.

In diabase, composed mainly of feldspar and augite, epidote and chlorite were formed [Fig. 3, Table 3], i.e., minerals [close] in com-position to those of the original rocks. There was almost no addition or subtraction of material. The feldspars in the diabases were albitized, as a rule, and the soda content of the endoskarns is high (Table 3).

In spessartites, composed of hornblende, feldspars and augite; actinolite, epidote and chlorite were formed, i.e., minerals chemically similar to the primary ones. Hence, there is a very slight difference be-tween the content of oxides in the primary rock, spessartite, and the endo-skarn, a chlorite-epidote rock (Fig. 4).

A certain peculiarity in the behavior of the oxides in the outer contact zone is observed in pyroxene lamprophyres (Fig. 2). The figures and tables show a substantial loss of silica and alumina from the pyrox-ene lamprophyres. They went into the creation of exoskarns. Large amounts of lime brought in from the limestone were used up in the forma-tion of endoskarns.

Summary

1. In the process of skarn formation at the Tabusklak deposit, sub-stantial amounts of SiO_2, Al_2O_3 and Fe_2O_3 were introduced with postmagmatic solutions, rather than contributed by the igneous rocks in the course of bimetasomatism. The latter mechanism has been described by Korzhinskii (1953) for a number of cases with similar geological settings. On the other hand, our endorsement of post-magmatic metasomatism is in agreement with the conclusions of Karpova and Ivashentsov (1954).

2. The introduction and removal of the main skarn-forming components (SiO_2, Al_2O_3, CaO) are observed in the outer contact zones but are incon-spicuous at the inner contacts. Therefore, the chemical composition of endoskarns depends almost entirely on the composition of the intrusives, while that of the exoskarns is determined by addition and subtraction of the main skarn-forming constituents.

3. The composition of the exoskarns is the same for all igneous rocks, but each igneous rock is characterized by a specific assemblage of endo-skarn minerals. Granodiorite porphyries are characterized mainly by pyroxene, garnet (rarely idocrase), followed by epidote, chlorite, quartz, and calcite; pyroxene lamprophyres, by uralite, followed by epidote, chlorite, quartz, and carbonate; spessartites, by actinolite, pyroxene pseudomorphs after amphibole, albite, then epidote, chlorite, quartz, and carbonate; kersantites, by epidote, chlorite, quartz, carbonate; diabases, by epidote, chlorite, quartz, and carbonate.

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VSEGEI.

DISTRIBUTION OF BORON IN ROCKS AND SKARN MINERALS OF THE VADIMO-ALEKSANDROVSK DATOLITE LOCALITY (TUR'IN MINERALIZED AREA, NORTHERN URALS)

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One of the important problems in studying the processes of ore deposition at a given locality is the determination of the characteristics of distribution of the main element of the ore among the rocks of the deposit. These characteristics make it possible, sometimes, to determine the source of the element, to judge of its behavior in the postmagmatic processes which took place at the locality, and often to establish the genetic connection between mineralization and certain intrusives.

We studied the distribution of boron in the rocks of the Vadimo-Alexandrovsk datolite deposit in the Northern Urals. The deposit lies on the eastern limb of the Tur'insk syncline in the Middle Devonian metasedimentary and extrusive rocks. These rocks are intruded by Variscan gabbros, gabbro-diorites, and quartz diorites and cut by diorite porphyry and lamprophyre dikes.

The metasedimentary complex is composed of massive white calcitic marble, tentatively assigned to the Eifel stage, and gray platy limestones lying conformably upon it. The limestones contain rhythmically alternating layers of calcareous-siliceous and calcareous-argillaceous shales changed into hornfelses. This sequence, tentatively referred to the Givetian stage, contains also beds of tuff and andesite flows. Skarns are widespread in the mineralized area; they are: garnet, pyroxene-garnet, epidote, pyroxene (sahlite) and, less frequently, wollastonite, and garnet-wollastonite skarns. They occur mainly in the contact zones of the massive intrusives and diorite porphyry dikes, but also form vein-like bodies in the limestones. Both limestones and siliceous rocks have been changed into skarns. The zoning of the skarns, at the deposits, intrusive -- desilicated near-skarn rock -- pyroxene-garnet skarn -- garnet skarn -- sahlite (or wollastonite) skarn -- limestone, corresponds in general to the pattern established by D.S. Korzhinskii [1] for the entire mineralized area.

The complete sequence of zones is seldom found, because of the intensive growth of the skarn zones. The epidote skarns, formed mainly during the lower temperature stage of equilibrium, replaced garnet skarns and

rnfelses and also developed at the contacts between the intrusives and
e garnet skarns.

Boron was determined spectrographically by using special boron-free
ectrodes. We described this method in detail in an earlier paper [2].

Igneous Rocks

We described the igneous rocks in a previous work. We showed that all
:rusive rocks have a constant boron content, ranging from 0.002 to
003%. Some of the extrusive rocks contain from 0.005 to 0.006% of
ron. Thus, the igneous rocks of the deposit have a higher boron content
ın the average for rocks of these types. This is characteristic of rocks
sociated with endogenous boron mineralization [3].

The Metasedimentary Complex

At the deposit and in the mineralized region as a whole, there are no
metamorphosed limestones and shales, and it is impossible, therefore,
judge of the boron content in the original sediments. The available data
re obtained from marbles and hornfelses.

The white massive limestones
the Eifel stage contain no boron.
alyses of the gray Zhivetian
ıestones showed the presence of
001% of boron in only two sam-
s. It has been stated by V.M.
ldschmidt [4] and T.G. Sahama
that very low boron content,
ım 0.0003 to 0.001% is charac-
istic of limestones. Evidently
:tamorphism had no sensible ef-
:t on the migration of boron.
The hornfelses occur in rhyth-
cally laminated layers among
ı gray limestone beds. Their
ckness varies from 1 cm to
-15 cm. Their mineralogical
ınposition, pyroxene, plagioclase
$_{30-38}$ and quartz, indicates
ıt the original shales were rich
CaO and SiO$_2$ and poor in alu-
na. These hornfelses approxi-
ıte Goldschmidt's types 8 and 9
scribed from the Oslo region [6].
ıny thin sections, as noticed
rlier by Korzhinskii, show nu-
rous sponge spicules filled with

Table 1

No. of sample	Locality	Boron content, %
0550	Hole 529, depth 80 m.	0.005
090	Hole 525, depth 117 m.	0.008
0142	same depth 190 m.	0.005
BA-0572	Hole 578, depth 76 m.	0.002
BA-0531	Hole 589, depth 112 m.	0.004
0174	Hole 525, depth 289 m.	0.004
0552	Hole 529, depth 88 m.	0.003
0553	same depth 89 m.	0.003
BA-0557	Hole 589, depth 312 m.	0.004
	Average	0.004

ırtz. According to Korzhinskii, these hornfelses were formed from
.careous-siliceous and calcareous-argillaceous sponge-bearing shales.
ε principal datolite mineralization is in these hornfelses within the skarn zone.

Only pure hornfelses untouched by the skarn-forming processes were used for analysis. The absence of datolite from them was checked microscopically.

Table 1 shows that the boron content of the hornfelses ranges from 0.002 to 0.008% and is 0.004% on the average. The form in which boron present in the hornfelses is not clear. It may be present in the form of ultramicroscopic tourmaline crystals undeterminable in thin sections or a a diadochic element in the plagioclase which is an essential mineral of the hornfelses. The last possibility was mentioned by V. L. Barsukov [7] an by us in a previously published paper.

Because of the absence of unmetamorphosed shales, it was impossible to discover whether the boron in the hornfelses was primary, i.e., deriv from the sediments, or whether it was introduced from the magma during contact metamorphism. Nor was it possible to determine whether or not part of the boron was removed from the shales during metamorphism, although the possibility of such removal is mentioned by Landergren [8]. Goldschmidt's investigations show that ancient marine argillaceous sediments contain 0.03% B, on the average, and siliceous sediments, up to 0.003% B. It is interesting that among all marine organisms corals and sponges contain the most boron in their skeletal structures.

According to A. P. Vinogradov [9] and Goldschmidt, the boron content in sponges is as follows:

	B content in %
Euspongia	0.17
Aphrocoleistus bocagei	0.03
Spongia (commercial sponge)	0.17

If it is assumed that the capacity to absorb boron from sea water is common to all sponges, then it may be assumed that the boron in the horn felses containing relicts of sponge spicules was not introduced from the magma. This is confirmed by the extreme rarity (near absence) of tourmaline in the deposit, indicating low concentration of boron in the magma.

Table 2

No. of sample	Locality	Boron content, %
0146	Hole 525	0.005
0203	"	0.002
0325	"	0.001
0334	"	0.003
0341	"	0.020
0342	"	0.020
0352	"	0.002
0498	"	0.007
0500	"	0.006
	Average	0.008

The Near-Skarn Rocks

At the contact with skarns the intrusives undergo metasomatism consisting of partial removal of SiO and addition of CaO. These rocks are usually composed of basic plagi oclase and a small amount of secondary diopside. The plagioclase i usually more calcic than in the unmetamorphosed rocks. According to Korzhinskii, it is bytownite, but according to E. S. Fedorov, it is anorthite.

The analysis (Table 2) show that in the process of metasomatism nei the skarns the rocks are somewhat enriched in boron, although in som samples the boron content does not differ from that of the unmetamorphos

ks. An increase in boron content in a number of samples may be ex-
ined by diminution in the amount of dark minerals and the presence of
re calcic plagioclase. This agrees with Barsukov's data on the relation
ween boron and the anorthite component of the plagioclase.

The Garnet Skarns

The garnet skarns are the most widespread in the deposit. They form
her thick zones at the contact with massive intrusives and thin zones at
tact with diorite porphyry dikes, and they occur also in vein-like bodies
the limestones. By means of refractive index determinations in liquids
high refractive index, kindly made by A. A. Yaroshevskii, and the deter-
nation of specific gravity, it was possible to establish that the majority
garnets are either near andradite in composition (87-90% andradite) or
e of intermediate type (48-50% andradite). Grossularite garnets (20-29%
dradite) are less common.

For boron determinations, the garnets were carefully picked under a
ocular microscope, pounded (not ground) into fragments up to 0.25 mm
diameter, and boiled for a short time in concentrated hydrochloric acid
insure removal of datolite.

Table 3 shows that most of the
alyzed garnets contain no boron.
e absence of boron in garnets does
depend on whether it is endoskarn
exoskarn garnet. Boron has been
nd in both endoskarn garnets (sp.
41) and exoskarn garnets (sp. 044).

Table 3

No. of sample	Locality	Boron content, %
044	Hole 525	0.002
073	"	none
0114	"	none
0213	"	none
0334	Hole 531	traces
0338	"	none
0341	"	0.005
0496	Hole 515	none
BA-0509	Hole 585	none
BA-0512	"	none

The Garnet-Wollastonite and Wollastonite Skarns

These skarns developed in the
rnfelses and gray limestones ex-
sively. Wollastonite occurs in
n fibers and in radiated fibrous
gregates. It replaces hornfelses and, to a less extent, limestones.
rnet clearly replaces wollastonite. It forms small spots and veinlets in
mass of wollastonite. Sometimes it completely replaces wollastonite.
e garnets are usually near andradite in composition (71-96% andradite);
ss commonly, they are of the intermediate type (40% andradite).
Monomineralic fractions of wollastonite and garnet from these skarns
re analyzed. The analyses are given in Tables 4 and 5.
The analyses show that the wollastonites contain, on the average, 0.009%
and garnets, 0.04% B.
According to M. Bertolani [10], the content of boron in bustamite is
006% and in andradite from Arendal, 0.04%.
In considering the mode of occurrence of boron in wollastonite and garnet
m the garnet-wollastonite skarn, we bore in mind the presence of datolite
these rocks in a very intimate association with these minerals and espe-
lly with wollastonite. We frequently observed microscopic crystals of

Table 4

Wollastonites

No. of sample	Locality	Boron content, %
0248	Hole 531	0.003
0362	Hole 541	0.02
BA-0528	Hole 589	0.001
BA-0543	"	0.02
BA-0551	"	0.004
BA-0553	"	0.02
BA-0554	"	0.002
BA-0556	"	0.004
Average		0.009

Table 5

Garnets

No. of sample	Locality	Boron content, %
036	Hole 525	0.05
037	"	0.10
033	"	0.06
0240	Hole 531	0.01
0254	"	0.01
0360	Hole 541	0.06
0361	"	0.03
BA-0574	Hole 578	0.03
Average		0.04

datolite at contacts between wollastonite crystals, and even pseudomorphs of datolite after wollastonite. In the case of garnets, datolite is easily removed by boiling in hydrochloric acid. But this method cannot be used with wollastonite, which is decomposed by the acid. The similarity of specific gravity of the two minerals makes it impossible to separate them in heavy liquids.

To determine how boron occurs in wollastonite, a phase x-ray structural analysis was made (by K. V. Fedotova). It showed that wollastonite contains admixed datolite. No such admixture was found in garnet, although a specimen with the highest boron content, of 0.1%, was analyzed by this method.

To confirm this result, an artificial mixture of boron-free garnet and datolite in proportions strictly corresponding to the boron content of 0.1% was subjected to phase analysis. The powder photograph revealed the presence of datolite.

Thus, it may be assumed that boron enters diadochically into the lattice of the analyzed garnet. It should be noted also that there is no connection between the composition of the garnets and their boron content.

The Epidote Skarns

The epidote skarns usually form at the lower temperature stage of equilibrium, replacing garnet skarns. Sometimes they form at the contact between the intrusive and the garnet skarn, replacing both. Locally, they replace hornfels. Epidote is also the main omponent of epidosites developed mainly at the expense of tuffs and extrusive rocks. Measurement of the refractive indices of the epidotes showed that the content of the iron-silicate component varies from 15 to 24%.

The analyses of the epidotes from the skarns show boron content ranging from 0.002 to 0.003% in most of the samples. No boron was found in the epidotes from the epidosites (sp. No. 016 and 051).

Analyzing these data, we see that in the process of formation of the

epidote skarns a certain amount of boron is introduced and fixed in the epidote. The concentration of boron in idocrase (viluite) is 0.12 to 1%, according to M. Bertolani, V.V. Mel'nitskii and Wherry and Chapin [11], and according to A.G. Betekhtin [12], may reach 3%. Epidote is structurally similar to idocrase, it is also an ortho-diorthosilicate, and it is probable that boron fixation is to be expected in it.

Table 6

No. of sample	Locality	Boron content, %
0127	Hole 525	0.002
0132	"	0.002
0191	"	0.003
0368	Hole 541	none
0489	Hole 515	0.002
BA-0500	Hole 585	0.002
BA-0509	Hole 585	0.003
016	Hole 525	none
051	"	none
Average		0.002

The analyzed epidotes do not have higher boron content as compared with Bertolani's data (0.002--0.003%).

The pyroxene (sahlite) skarns are completely devoid of boron.

Of the products of low temperature metamorphism, the chlorites developed after garnets were analyzed. No boron was found in them.

An examination of the results leads to certain conclusions concerning the behavior of boron during the formation of skarns at our locality. The absence of boron-bearing skarn minerals at all stages of skarn formation indicates that during this process boron was a completely mobile component and that its chemical potential was low. During the process of formation of the near-skarn rocks, no boron was contributed by the intrusives. The slight increase in the boron content in the near-skarn rocks, as has already been pointed out, is due to the increase in the amount of calcic plagioclase. In the replacement of the near-skarn rocks and hornfelses by garnet, boron passed into solution and in most cases was not fixed in garnets, probably because of its low concentration during the high temperature stage of skarn formation. During the formation of sahlite and wollastonite skarns, boron behaved in an analogous way.

During the development of skarn zones and, in particular, during the replacement of wollastonite skarn by garnet skarn, boron became somewhat more concentrated in the solution and entered into the garnet lattice. Korzhinskii [13] states that the increase in the concentration of a mobile component in the solution changes the paragenesis and causes the formation of minerals enriched in this component. This agrees entirely with the fact that the earlier garnets are boron-free, while the later ones (from garnet-wollastonite skarns) are boron-bearing.

With decrease in temperature, the activity of boron in solutions increases. During the stage of formation of epidote skarns, part of the boron entered into epidote, but its concentration in the solutions was still too low to form independent minerals.

During the low temperature stage, marked by the formation of sericite and chlorites, boron does not enter diadochically into the lattices of these minerals, as confirmed by its absence from the chlorites and the crystallochemical deductions of Barsukov. At this stage, boron becomes fixed in the form of datolite.

It should be noted that datolite forms only by replacing siliceous rocks and silicates, but not in pure limestones. This indicates that the formation

of datolite requires only an addition of boron, the silica being derived from the replaced rocks.

All this suggests that datolite mineralization may occur only in those skarn localities where limestones with siliceous material are present (siliceous limestones, marls, limestones with siliceous partings).

The observations at the Vadimo-Aleksandrovsk deposit do not confirm the hypothesis of Barsukov and Egorov [14] that boron is removed from garnets during the stage of epidotization and fixed in datolite. The epidotization of the garnets is accompanied by a certain addition of boron, and our observations show that datolite is never intimately associated with epidote, but appears much later, replacing it or forming veinlets.

Our data suggest that, in general, the absence of boron from garnets is not an unfavorable sign in evaluating boron concentration in datolite-bearing skarn localities, while relatively high boron content in garnets is undoubtedly an important geochemical evidence and guide to datolite mineralization.

Summary

1. At the deposit, boron is concentrated in hornfelses in garnets from the garnet-wollastonite skarns, in epidotes and also in igneous and near-skarn rocks.

2. The enrichment of the argillaceous and siliceous sediments in boron and the high boron content of sponge spicules suggest that the boron in the hornfelses formed from the calcareous-argillaceous and calcareous-siliceous spicule-bearing shales is primary and not a contribution from the magma.

3. During the process of near-skarn alteration, no boron is contributed by the igneous rocks.

4. The presence of boron in wollastonites is due to a mechanical admixture of datolite.

5. The garnets from the garnet skarns do not, as a rule, contain boron.

6. The process of epidotization is accompanied by an addition of boron and its fixation in epidote.

7. The absence of boron skarn minerals is explained by the facts that in the process of skarn formation boron behaves as a completely mobile component and that its chemical potential is low.

8. The formation of datolite is favored by the presence of siliceous material in the limestones. Only boron is added during the formation of datolite, and not silica.

9. The absence of boron from garnet skarn zones is evidently not a criterion for judging of the presence of datolite in the skarns. The relatively high boron content in garnets, on the other hand, is an important geochemical criterion and guide to datolite mineralization.

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DISTRIBUTION OF GALLIUM
IN THE ROCKS OF THE SOVIET UNION

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Gallium is one of the typical dispersed elements. According to the latest published data [1], its average content in the rocks of the earth's crust is 0.0015% by weight, i.e., it is about equal to the content of lead and is higher than the average content of arsenic, molybdenum, or tungsten, elements which form independent minerals and accumulate in the form of large deposits. Thus, gallium is a relatively abundant element, but it forms no independent minerals, let alone deposits. As a dispersed element, it enters into the composition of numerous minerals and rocks, owing to the close resemblance of its chemical and crystal-chemical properties to those of aluminum. According to V.M. Goldschmidt [2, 3], gallium, whose ionic radius is near that of aluminum, is easily "camouflaged" in the lattices of aluminum minerals. It is possible also that gallium may diadochically replace Fe^{3+} (0.67A), Cr^{3+} (0.64A) and Ti^{4+} (0.64A). Moreover, being slightly more electronegative than aluminum (Ga--1.6, Al--1.5, according to Pauling [4]), gallium may enter into the silicon-oxygen tetrahedra, and this, apparently, explains its presence in non-aluminous orthosilicates (olivine, hypersthene, diopside). Unlike aluminum, gallium exhibits three different modes of behavior. Its association with aluminum, and to some extent with ferric iron (hematite, magnetite, non-aluminous garnets, etc.) indicates that it is lithophile. It is also frequently present in sulfides, its content in sphalerite is up to 0.4%, and it occurs in trace amounts in galena, pyrite, bismuthinite, and other sulfides. The highest gallium content has been found in germanite (0.75%) from Tsumeb (South-West Africa). The usual presence of gallium in iron meteorites indicates that it is also siderophile.

Weathering processes result in further dispersion of gallium, because its ion is so much more mobile than the aluminum ion.

The geochemistry of gallium has received much attention. As early as 1897, Hartley and Ramage [5] pointed out the relation between gallium and aluminum in feldspars, bauxites, and clays. The most thorough investigation of the behavior of gallium in nature was made by Goldschmidt and his associates, who showed that there is an intimate relation between gallium and aluminum in silicates, that the Ga/Al ratio increases from basic to siliceous and alkalic rocks and that gallium is enriched in rest magmas. Later, these authors [6] published data on the gallium content in German

ranites, gabbros, shales, and greisen. A very complete compilation on he distribution of gallium was given in 1937 by Einecke [7] and confirmed he accumulation of gallium in rest magmas. In 1938, Van Tongeren [8] nvestigated the distribution of gallium in the rocks of the East Indies and btained higher values for its content than those reported from other re- gions. He explained this by the peculiarities of formation of the young ntrusives of the archipelago.

Later, a number of investigators [9, 10, 11], in studying the products f differentiation of gabbroic magma, established that gallium is rather niformly distributed through the various differentiates and that there is no ccumulation of gallium in the products of crystallization of the rest magma acid rocks, aplites, and pegmatites). Shimer [12] came to the same con- lusion after comparing pegmatitic and normal rock-forming minerals of New England. There are data on the distribution of gallium in the works of Ahrens [13, 14], Sandell [15] and other investigators [16, 17, 18, 19]. All of these studies indicate considerable uniformity in the distribution of gallium in rocks and the impossibility of using it as an indicator of proc- esses. Little has been published on the distribution of gallium in rocks, ores, and minerals of the Soviet Union.

The enrichment of micas in gallium was mentioned by Vernadskii [20] in 1910. Detailed discussions of the geochemistry of gallium appeared in the works of S.A. Borovik, V.V. Shcherbina, N.V. Lizunova and others [21, 22].

A recently published paper by G.G. Vorob'ev [23] on the distribution of gallium in the rocks and minerals of Mongolia should be mentioned. The paper cites gallium content 3 to 5 times as high as that given by the majority of other investigators. Vorob'ev believes this to be in conformity with the youth of this geological province and considers Mongolia one of the rare gallium provinces. It seems to the writer that the existence of such a rich 'gallium province" is improbable, especially if the geochemical properties of gallium and its intimate association with aluminum are taken into con- sideration. Gallium is very uniformly distributed among the principal ig- neous rocks. Regional enrichments in gallium do occur, but they are due in all cases either to the presence of pegmatites in the area or to super- imposed postmagmatic processes. The presence of a considerable enrich- ment throughout a rather extensive igneous terrain is doubtful. Vorob'ev's reference to Van Tongeren's data is not convincing, because Van Tongeren admits that his high results may be due to analytical variations.

The present article is based on 1500 analyses of different rocks and the principal rock-forming minerals of the Soviet Union.

To obtain the average content of gallium in individual regions, average samples (mixed samples) of the representative rocks were prepared by mixing two-gram samples of rocks powdered in an agate mortar.

The rocks and minerals were analyzed for gallium by a spectrographic technique developed by the author [24]. The results obtained by this tech- nique were checked by Sandell's fluorimetric method [25] and colorimetri- cally by V.S. Saltykova and E.A. Fabrikova [26]. All three methods showed good agreement. The colorimetric method gives slightly higher values (by 20-25%). The standards used in the spectrographic analysis were checked by the international standard, Granite G-1. The sensitivity of the method is 10%.

The analyses for aluminum and silicon were made spectrographically, using hundred-fold dilution with zinc oxide [27]. As an additional check, some of the samples were analyzed chemically.

Gallium in Ultrabasic Rocks

Rocks containing less than 45% SiO_2 were considered ultrabasic. Their gallium and aluminum content is given in Table 1.

Table 1

Gallium Content in Ultrabasic Rocks

Name of rock	Number of samples	Region	Ga,%	Al,%	Ga/Al · 10^{-4} weight ratio	Ga/Al atomic ratio
Olivinite	5	Kola Peninsula, Sal'nye tundry	0.0001	0.75	1.2	1:20000
Peridotite	10	Same	0.0003	2.8	1.1	1:25000
Serpentinized peridotite	5	"	0.0003	2.9	1.0	1:26000
Feldspathic pyroxenite	10	"	0.0005	4.2	1.1	1:25000
Peridotite	5	Caucasus	0.0003	2.8	1.1	1:25000
Serpentinized dunite	5	Ural Mts., Cherem-shanka	0.0001	1.1	1.0	1:26000
Serpentinite	5	Same	0.0001	–	–	–
Kimberlite	10	Eastern Siberia, Yakutia	0.0001	0.98	1.0	1:26000
Serpentinite	5	Enisei Range	0.0001	–	–	–
Pyroxenite	10	Eastern Sayan Mts.	0.0003	2.95	1.0	1:26000
Serpentinite	5	Same	0.0001	–	–	–
		Average	0.0002	2.1	1.0	1:26000

An examination of these data shows that all ultrabasic rocks contain gallium except the serpentinites of the Urals and the Enisei Range, in which gallium content is below the sensitivity of the method. The highest gallium content was found in the feldspathic pyroxenite of the Kola Peninsula, containing up to 5% plagioclase. The content of gallium in ultrabasic rocks is determined mainly by the content of aluminum, and the Ga/Al ratio in all rocks is practically constant.

Let us examine the distribution of gallium among the essential rock-forming minerals, using peridotite and pyroxenite as examples (Table 2).

Gallium occurs in pyroxenes, especially in augite, the aluminous variety of pyroxene, in amphiboles (hornblende) and in plagioclase. The presence of gallium in non-aluminous pyroxenes (hypersthene, enstatite, diopside) may be explained, on the one hand, by the imperfect separation of

Table 2

Gallium Content in the Minerals of Ultrabasic Rocks

Mineral	Percent of mineral in the rock	Ga content in the mineral, %	Contribution of the mineral to the Ga content in the rock, %	Ga content in the rock, %
Peridotite (Urukh and Psygan-Su rivers interfluve, Caucasus)				
Olivine	15	–	–	
Pyroxenes	10.0	0.0003	0.00003	
Amphibole (hornblende)	73.4	0.0004	0.00029	
Total	98.4		0.00032	0.0003
Feldspathic pyroxenite (Sal'nye tundry, Kola Peninsula)				
Clinopyroxene	75.0	0.0003	0.00022	
Orthopyroxene	10.0	0.0004	0.00004	
Amphibole	4.5	0.0008	0.00004	
Plagioclase	9.2	0.0011	0.00010	
Total	98.7		0.00040	0.0005

these minerals and by the presence of microscopic aluminum-bearing inclusions in them, and, on the other, by the possible replacement of silicon by gallium in the silicon-oxygen tetrahedra.

Gallium in Basic Rocks

Rocks containing less than 55% SiO_2 were referred to the basic group (gabbro, diabase, basalt, etc.). The gallium and aluminum content and the Ga/Al ratios in these rocks are given in Table 3.

The gallium content in basic rocks varies considerably. The variation in the absolute gallium content may be explained by variation in the mineralogical composition of the rocks and their aluminum content. If the gallium content were proportional to the aluminum content, the Ga/Al ratio would remain constant in passing from one variety of rock to another. The table shows, however, that it varies considerably (from 1.5 to 2.5), and this cannot be ascribed to errors of analysis. The melanocratic rocks contain less gallium than the leucocratic rocks, because of their lower plagioclase content. A high Ga/Al ratio and a relatively low gallium content are observed in the gabbro-norite from Northern Karelia, which is composed mainly of pyroxenes (50%) and labradorite (20%). The gallium content in labradorite is normal, but in the pyroxenes it is rather high whereas the aluminum content is low. Evidently in the pyroxenes, gallium substitutes not only for aluminum but also for ferric iron. The $Ga/Al + Fe^{3+}$ ratio is 1:9.

Table 3

Gallium Content in Basic Rocks

Name of rock	Number of samples	Region	Ga, %	Al, %	Ga/Al · 10^{-4} weight ratio	Ga/Al atomic ratio
Melanocratic gabbro	10	Kola Peninsula, Sal'mye tundry	0.0011	6.9	1.6	1:16000
Gabbro-norite	10	Northern Karelia	0.0015	5.8	2.5	1:10000
Olivine gabbro	5	Ukraine, Zhdanovsk ore deposit	0.0009	6.0	1.5	1:17000
Gabbro	5	same	0.0016	8.0	2.0	1:14000
Basalt	5	Crimea, Bodrak River	0.0017	8.5	2.0	1:13000
Gabbro	5	Caucasus, Suganski Range	0.0020	8.9	2.2	1:11000
Gabbro-diorite	10	Caucasus, Meriz intrusive	0.0014	7.4	1.9	1:15000
Diabase gabbro	10	Caucasus, Sanchar massif	0.0018	8.4	2.1	1:12000
Gabbro	5	Ural Mts., Kuznechikha	0.0012	8.0	1.5	1:17000
Gabbro with eutectic texture	1	Ural Mts., Degtyarka	0.0012	7.6	1.6	1:16000
Amphibolite	3	Khakassiya, Kuznetskii Alatau	0.0019	8.9	2.1	1:12000
Gabbro	5	Kazakhstan, Ulu-Tau, Atabul	0.0019	8.8	2.2	1:11000
Gabbro-amphibolite	15	Kazakhstan, Eskuly	0.0018	8.4	2.1	1:12000
Diabase	5	Kazakhstan, Sary-Su-Tengiz watershed	0.0018	8.0	2.2	1:11000
Basalt porphyry	3	Same	0.0015	7.4	2.0	1:13000
Gabbro-diorite	5	"	0.0011	7.2	1.5	1:17000

Table 3 (Cont'd.)

Gallium Content in Basic Rocks

Name of rock	Number of samples	Region	Ga, %	Al, %	Ga/Al · 10^{-4} weight ratio	Ga/Al atomic ratio
Melanocratic gabbro	1	Eastern Sayan Mts.	0.0011	7.3	1.5	1:17000
Traps	50	Eastern Siberia	0.0019	7.8	2.4	1:10500
Diabase gabbro	25	Enisei Range	0.0014	7.5	1.9	1:15000
Basalt	5	Kamchatka	0.0020	8.4	2.3	1:10000
Andesite-basalt	5	Same	0.0018	9.0	2.0	1:11500
		Total	0.0015	8.3	1.8	1:15000

Table 4

Gallium Content in the Minerals of Basic Rocks

Mineral	Percent of mineral in the rock	Ga content in the mineral, %	Contribution of the mineral to the Ga content in the rock, %	Ga content in the rock, %
Gabbro of the Suganskii massif (Caucasus)				
Olivine	–	–	–	
Pyroxene	5.2	0.0001	0.00005	
Plagioclase (labradorite)	65.8	0.0025	0.00165	
Amphibole	29.1	0.0010	0.00030	
Biotite	A few flakes	–	–	
Total	100.1		0.0020	0.0021
Melanocratic gabbro of the Sal'nye tundry (Kola Peninsula)				
Olivine	5.0	–	–	
Pyroxene	74.8	0.0006	0.00045	
Plagioclase (bytownite)	20.2	0.0020	0.00044	
Amphibole	A few crystals	–	–	
Total	100.0		0.0009	0.0010

The same may be said of the traps, which contain up to 6% Fe_2O_3.

The distribution of gallium in the minerals is given in Table 4. The minerals were first separated by heavy liquids, then into magnetic and electromagnetic fractions and, finally, hand-picked under a binocular microscope. The clinopyroxenes were not separated from the orthopyroxenes because of the great difficulty involved in their separation.

The table shows that gallium is concentrated mainly in the plagioclases and to a much smaller degree in amphiboles and pyroxenes. On the average, the minerals of basic rocks contain more gallium than the same minerals in the ultrabasic rocks. This increase is not significant in the case of amphiboles and pyroxenes, but the plagioclases of basic rocks contain from 2 to 2.5 times as much gallium as the plagioclases of ultrabasic rocks, in spite of the close similarity in their chemical composition (labradorite, bytownite).

Gallium in Intermediate Rocks

This group includes rocks with SiO_2 content from 55 to 65% (syenites, diorites). Fresh, little altered samples were taken for analysis. The gallium and aluminum content and the Ga/Al ratios are presented in Table 5.

The variations in the gallium content in the intermediate rocks are the same as in the basic rocks (from 0.0010 to 0.0023%) although the mineralogical composition of these rocks varies within narrow limits. Although every attempt was made to select fresh specimens for the preparation of average samples, some regions are represented by strongly weathered rocks (Crimea, Urals). These weathered rocks contain the smallest amounts of gallium and have the lowest Ga/Al ratios (1.5 --1.6). High gallium content and Ga/Al ratios were found in syenites from the regions of alkalic intrusions (Ukraine) and in the freshest rocks from the regions of the relatively young intrusives (Caucasus, Central Kazakhstan).

The distribution of gallium in the minerals is given in Table 6. The hornblendes and pyroxenes contained in the electromagnetic fraction were analyzed together because of the difficulty of separating them. The potassium feldspar was separated from the plagioclase by its color under the binoculars.

As in the basic rocks, the main mass of gallium is concentrated in the plagioclases, but in the intermediate rocks there appears a new carrier of gallium, the red potassium fledspar. The lowest gallium content is found in the dark minerals, hornblendes and pyroxenes. Quartz, which is present in some rocks, does not contain gallium.

Gallium in Acid Rocks

This group of rocks is most completely represented in the present work because it is so widespread. All rocks with more than 65% SiO_2 (granodiorites, tonalites, adamellites, granites, etc.) are included in this group, as well as the ultra-acid rocks with over 75% SiO_2 (aplites). The granitoids of the Meriz intrusion in the Caucasus are represented by an average sample composed of 25 samples of granites and granodiorites. The other

Table 5

Distribution of Gallium in Intermediate Rocks

ame of rock	Number of samples	Region	Ga, %	Al, %	Ga/Al · 10^{-4} weight ratio	Ga/Al atomic ratio
yroxene syenite	5	Kola Peninsula	0.0017	8.2	2.1	1:12000
yenite	10	Ukraine, Zhdanovsk ore deposit	0.0023	9.9	2.3	1:10500
iorite	5	Crimea, Boorak River	0.0010	–	–	–
ndesite	5	Crimea	0.0010	6.1	1.6	1:16000
ine-grained liorite	10	Caucasus, Suganski Range	0.0015	7.9	1.9	1:15000
iorite	5	Caucasus Meriz intrusive	0.0022	8.9	2 5	1:10000
yenite-liorite	5	"	0.0017	8.6	1.9	1:15000
iorite	5	Ural Mts., Degtyarka	0.0013	8.0	1.6	1:16000
yenite	10	Khakassiya	0.0017	8.1	2.1	1:12000
iorite	15	Kazakhstan, Sary-Su-Tengiz watershed	0.0016	8.4	1.8	1:15000
yenite	15	"	0.0020	8.5	2.4	1:10000
iorite	5	Eastern Siberia	0.0018	8.3	2.2	1:11000
iorite	10	Central Tien Shan (Kirgiziya)	0.0020	8.9	2.2	1:11000
ornblende syenite	10	"	0.0017	8.2	2.1	1:12000
ndesite	8	Kamchatka	0.0017	8.6	1.9	1:15000
lelanocratic syenite	10	Taimyr Peninsula	0.0015	8.4	1.6	1:16000
eucocratic yenite		"	0.0012	6.9	1.7	1:16000
		Average	0.0016	8.6	1.9	1:15000

erage samples are composed of rocks of a single type similar in chemical nposition. The distribution of gallium and the Ga/Al ratios for the acid cks are given in Table 7.

Table 6

Gallium Content in the Minerals of Intermediate Rocks

Mineral	Percent of mineral in the rock	Ga content in the mineral, %	Contribution of the mineral to the Ga content in the rock, %	Ga content in the rock, %
Hornblende diorite (Suganskii massif, Caucasus)				
Amphibole (hornblende)	35.2	0.0016	0.00057	
Plagioclase (labradorite)	54.7	0.0020	0.00110	
K feldspar	10.1	0.0012	0.00012	
Biotite	A few flakes	–	–	
Total	100.0		0.0018	0.0020
Leucocratic syenite (Khakassiya, Kuznetskii Ala Tau)				
Pyroxene / Amphibole	19.8	0.0010	0.00020	
Plagioclase (andesine)	60.2	0.0025	0.00150	
K feldspar	17.4	0.0015	0.00030	
Quartz	2.5	–	–	
Total	100.0		0.0020	0.0019

The variations in the gallium content are not very large (from 0.0015 to 0.0024%). The lowest gallium content was found in the granites of the Kola Peninsula (rapakivi), which are more basic than normal granites. The highest gallium content was found in the pegmatoidal granites of the Altai Mts. (Ubino-Belorechensk massif) and in Transbaikalia (in the very old granitic laccolith, Tsagan). The enrichment of the Tsagan granite in gallium is due, apparently, to postmagmatic alteration of the rock (potassium metasomatism). The average gallium content in the acid rocks $(1.9 \cdot 10^{-3}\%)$ agrees with the data of Goldschmidt $(2 \cdot 10^{-3}\%)$, Ahrens $(1.7 \cdot 10^{-3}\%)$ and Sandell $(1.7 \cdot 10^{-3}\%)$. On the average, granites and aplites contain more gallium than granodiorites. Still higher gallium content is found in two-mica granites. The Ga/Al ratios range from 2.1 to 3.5. The pegmatoidal Altai granite has the highest ratio. Regionally there is a considerable uniformity in the distribution of gallium. The rocks of the Altai Mts. and Transbaikalia are somewhat enriched in it. No significant variation in gallium content with the age of rocks was observed.

The distribution of gallium in minerals of the acid rocks is presented in Table 8 on the basis of four samples with different mineralogical composition and different gallium content. The minerals were separated by heavy liquids and then hand-picked under a binocular microscope. The separation of the potassium feldspar from the plagioclase was possible only when it had

Table 7

Distribution of Gallium in Acid Rocks

Name of rock	Number of samples	Region	Ga, %	Al, %	Ga/Al · 10^{-4} weight ratio	Ga/Al atomic ratio
Granite	8	Kola Peninsula	0.0014	6.9	2.1	1:11500
Granite	5	Northern Karelia	0.0017	7.3	2.4	1:11000
Granite porphyry	10	Caucasus, Suganskii Range	0.0019	7.4	2.6	1:10000
Two-mica granite	10	Caucasus, Urukh--Psygan-Su interfluve	0.0021	7.6	2.8	1:9000
Granodiorite	10	Same	0.0018	7.9	2.3	1:11000
Aplite	8	Same	0.0021	6.9	3.1	1:8000
Granitoids	25	Caucasus, Meriz intrusive	0.0018	–	–	–
Granite	25	Ural Mts., Arakul'	0.0020	7.9	2.6	1:10000
Granite	25	Ural Mts., Karabash	0.0016	7.2	2.2	1:11500
Granodiorite	15	Khakassiya, Kuznetskii Ala-Tau	0.0019	8.2	2.3	1:11000
Granite	20	Same	0.0023	7.6	3.0	1:9000
Granodiorite	15	Central Kazalhstan, Sary-Su-Tengiz watershed	0.0020	7.8	2 6	1:10000
Granite	10	Same	0.0022	7.4	3.0	1:9000
Leucocratic granite	3	Same	0.0017	7.1	2.4	1:11000
Granite porphyry	5	Central Kazakhstan	0.0018	7.2	2.5	1:10000
Granite porphyry	5	Transbaikalia, Adun-Chelon	0.0024	7.6	3.2	1:8000
Felsitic granite	5	Same	0.0020	7.3	2.9	1:9000
Granite	2	Transbaikalia, Tsagan	0.0027	7.5	3.5	1:7000

Table 7 (Cont'd.)

Distribution of Gallium in Acid Rocks

Name of rock	Number of samples	Region	Ga, %	Al, %	Ga/Al · 10⁻⁴ weight ratio	Ga/Al atomic ratio
Biotite granite	5	Altai Mts. Ubino-Belorechen-skii and Tigiretskii massifs	0.0018	7.1	2.9	1:9000
Two–mica granite	10	Same	0.0021	7.2	2.9	1:10000
Granite porphyry	2	Same	0.0017	6.9	2.5	1:10000
Pegmatoidal granite	2	Same	0.0030	7.9	3.8	1:6000
Granite	25	S. E. Tuva	0.0018	7.1	2.5	1:10000
Granodiorite	20	Kirgiziya, Tien Shan, Susamyr and Kirgiz Ranges	0.0016	7.6	2.1	1:12000
Granite	20	Same	0.0017	7.1	2.4	1:11000
Leucocratic granite	5	Same	0.0018	7.2	2.4	1:11000
Granite-aplite	10	Same	0.0022	6.9	3.2	1:8000
Granite	25	Eastern Siberia (Yakutia)	0.0020	7.1	2.9	1:9000
Granite	10	Enisei Range	0.0022	7.3	3.0	1:9000
Rhyolite	5	Kamchatka	0.0019	7.0	2.7	1:9500
Biotite granite	10	Taimyr Peninsula	0.0019	7.3	2.6	1:10000
		Average	0.0019	7.2	2.6	1:10000

a distinctive color or appeared in large phenocrysts. Separation of the potassium feldspar from the plagioclase in the groundmass was difficult and was not done.

The micas, muscovite and biotite, show the highest gallium content. The layered structure of the micas and the presence of aluminum favor the entry of gallium into the lattices of biotites and muscovites. The variations in the gallium content of micas may be explained by the presence of iron in some of them (biotites with high iron content have less gallium) and by the difference in the physicochemical conditions of their formation. In the granites which contain hornblende in addition to biotite, the former is characteristically

Table 8

Gallium Content in the Minerals of Acid Rocks

Mineral	Percent of mineral in the rock	Ga content in the mineral, %	Contribution of the mineral to the Ga content in the rock, %	Ga content in the rock, %
Granodiorite, Susamyr massif (Kirgiziya)				
Quartz	18.5	–	–	
Plagioclase	55.0	0.0021	0.00116	
K Feldspar	12.0	0.0012	0.00014	
Biotite	10.0	0.0045	0.00045	
Amphibole (hornblende)	4.5	0.0018	0.00008	
Total	100.0		0.0018	0.0017
Granite, Susamyr massif (Kirgiziya)				
Quartz	34.0	–	–	
Plagioclase (Oligoclase)	29.9	0.0022	0.00066	
K feldspar	32.3	0.0014	0.00045	
Biotite	3.7	0.0070	0.00027	
Total	99.9		0.0014	0.0014
Two-mica granite (Caucasus, Urukh -- Psygan Su interfluve)				
Quartz	35.0	–	–	
Plagioclase (albite and oligoclase)	35.0	0.0025	0.00087	
K feldspar	18.0	0.0015	0.00027	
Biotite	4.9	0.0055	0.00027	
Muscovite	7.0	0.0100	0.00070	
Total	99.9		0.0021	0.0022
Biotite granite (Southeastern Tuva)				
Quartz	29.0	0.0002	0.00006	
Plagioclase (oligoclase)	40.0	0.0024	0.00096	
K feldspar	20.0	0.0018	0.00036	
Biotite	9.8	0.0071	0.00070	
Total	98.8		0.0021	0.0021

enriched in gallium up to 0.005% and, as a rule, hornblende crystallized ate contains more gallium than the earlier hornblende. The potassium

Table 9

Distribution of Gallium in Alkalic Rocks

Name of rock	Number of samples	Region	Ga, %	Al, %	Ga/Al · 10^{-4} weight ratio	Ga/Al atomic ratio
Nepheline syenite	5	Kola Pen., Keivy	0.0062	11.3	5.6	1:4500
Khibinite	4	Kola Pen., Khibiny	0.0032	10.3	3.1	1:8000
Foyaite	4	"	0.0024	–	–	–
Mariupolite	15	Ukraine, Zhdanov ore deposit	0.0070	13.4	5.2	1:5000
Melanocratic syenite	10	"	0.0050	12.9	3.9	1:6000
Nepheline syenite	5	Ural Mts., Vishnevye Gory	0.0046	10.4	4.5	1:5500
Miaskite	10	Ural Mts., Miassy	0.0034	9.9	3.5	1:7000
Shonkinite	4	Central Kazakhstan	0.0018	5.1	3.6	1:7000
Nepheline syenite	10	"	0.0031	9.6	3.3	1:7500
Nepheline syenite	10	Central Tien Shan, Kirgiziya	0.0038	9.8	4.0	1:6000
Alkalic syenite	15	"	0.0024	8.3	3.0	1:8500
Monzonite	5	"	0.0022	7.2	3.0	1:8500
Nepheline syenite	10	S. E. Tuva	0.0043	10.1	4.3	1:6000
Monzonite	5	"	0.0024	8.2	3.0	1:8500
Nepheline syenite, leucocratic	25	Eastern Siberia, Enisei Range	0.0058	12.6	4.5	1:5500
Nepheline syenite, melanocratic	5	"	0.0038	12.3	3.1	1:1800
		Sakhalin	0.0040	10.1	4.0	1:6000
		Average	0.0040	9.9	4.1	1:6000

feldspars contain the same amount of gallium as the intermediate rocks, with microclines being richer in it than orthoclase. The gallium content in green microcline, amazonite, reaches 0.0100%. The presence of gallium in quartz is due, apparently, to the imperfect separation of it from the potassium fledspars present in the light fraction.

Gallium in Alkalic Rocks

Rocks of this group are subordinate in the earth's crust but they play important role in the geochemistry of gallium, and for this reason are eated here as a separate group. Included in this group are all varieties nepheline syenite available to the author, alkalic syenites and nepheline-aring rocks (shonkinites, monzonites).

Table 9 shows that the average gallium content in alkalic rocks is con-derably higher than in any of the preceding groups. The variation in gal-m content is quite large (from 0.0018 to 0.0070%). This is due mainly to e chemical and mineralogical composition of these rocks. The varieties ntaining much nepheline, sodalite, and cancrinite are usually enriched in llium. The more basic varieties (shonkinites, monzonites) contain small nounts of gallium (near the clarke amount). Basically, gallium content is ntrolled by the content of aluminum in the rock, and so the Ga/Al ratio ries only a little (from 3.0 to 5.0). The nepheline syenites of the Kola ninsula, the mariupolites of the Ukraine, and the leucocratic nepheline enites of the Enisei Range are relatively rich in gallium.

The distribution of gallium among the minerals of alkalic rocks is given Table 10.

The highest gallium content is found in sodalite and biotite, but its main ass is concentrated in nepheline and microcline although its content in ese minerals is lower. The presence of gallium in the alkalic pyroxene, girine, a non-aluminous mineral (analysis showed tenths of one percent ι), indicates the possibility of replacement of ferric iron by gallium.

A general summary of the distribution of gallium in the rocks of the viet Union is presented in Table 11.

Discussion of Results

The data on the distribution of gallium in the different types of rocks ow that it is somewhat irregular. The gallium content is lowest in the trabasic rocks and increases through basic, intermediate, and acid rocks the maximum content in the alkalic rocks.

The gallium content in the rocks is controlled mainly by the content of uminum, because gallium substitutes diadochically for aluminum in the ttices of the aluminosilicates. The close resemblance between the chemi-l properties of the two elements, members of the same group in the peri-lic table, and the nearness of their ionic radii make Goldschmidt's princi-es of "camouflage" effective. According to this principle, gallium, which is a larger ionic radius than aluminum, has a tendency to accumulate in e latest products of crystallization, i.e., in acid rocks, dikes, and pegma-es. This is confirmed by the work of Goldschmidt, Sandell, and others. it, on the other hand, the behavior of gallium must be studied in a massif lich shows clearly that all of its rocks are differentiates of a single magma. example of such a massif is the Skaergaard intrusive, whose geochemi-l characteristics have been studied by Nockolds, Wager, and others. Ac-rding to these authors, no accumulation of gallium in the products of ystallization of the rest magma is observed in this case and gallium is liformly distributed through all differentiates. The Ga/Al ratio is practi-ly the same in all rocks of this intrusive. That gallium has no tendency accumulate in rest magmas has also been pointed out by Shimer, who

Table 10

Gallium Content in the Minerals of Alkalic Rocks

Mineral	Percent of mineral in the rock	Ga content in the mineral,%	Contri.of mineral to Ga content in rock %	Ga content in the rock, %
Nepheline syenite (Enisei Range)				
Nepheline	35,0	0,0044	0,00154	
Microcline	51,0	0,0020	0,00102	
Albite	2,5	0,0054	0,00014	
Sodalite	3,2	0,0070	0,00022	
Aegirine	8,0	0,0019	0,00015	
	99,7		0,0031	0,0032
Nepheline syenite (Sandyk massif, Tien Shan, Kirgiziya)				
Nepheline	45,6	0,0035	0,00055	
K feldspar				
K feldspar	75,0	0,0015	0,00103	
Pyroxene	1,3	0,0024	0,00003	
Biotite	4,3	0,0068	0,00029	
Total	96,2		0,0019	0,0019

Table 11

Distribution of Gallium in the Rocks of the Soviet Union

Rocks / Region	Ultra-basic Ga, %	Ultra-basic Ga/Al · 10⁻⁴	Basic Ga, %	Basic Ga/Al · 10⁻⁴	Inter-mediate Ga, %	Inter-mediate Ga/Al · 10⁻⁴	Acid Ga, %	Acid Ga/Al · 10⁻⁴	Alkalic Ga, %	Alkalic Ga/Al · 10⁻⁴
Kola Pen.	0,0003	1,1	0,0011	1,6	0,0015	2,0	0,0014	2,2	0,0040	4,3
N. Karelia	—	—	0,0015	2,5	0,0016	2,1	0,0016	2,4	—	—
Ukraine	—	—	0,0013	1,8	0,0023	2,3	0,0022	2,9	0,0060	4,5
Crimea	—	—	0,0015	1,9	0,0010	2,0	—	—	—	—
Caucasus	0,0003	1,0	0,0016	2,1	0,0016	2,2	0,0020	2,7	—	—
Ural Mts.	0,0001	1,0	0,0012	1,6	0,0013	1,6	0,0016	2,4	0,0040	4,0
Central Ka-zakhstan	—	—	0,0018	2,0	0,0018	2,2	0,0021	2,8	0,0025	3,5
Taimyr Pen.	—	—	—	—	0,0014	1,7	0,0019	2,7	—	—
Kamchatka	—	—	0,0018	2,1	0,0017	1,9	0,0019	2,7	—	—
Sakhalin	—	—	—	—	—	—	0,0017	2,4	0,0040	4,0
East. Siberia	0,0001	1,0	0,0019	2,4	0,0019	2,5	—	—	—	—
Yakutiya	—	—	—	—	0,0018	2,2	0,0020	2,9	—	—
Enisei Range	0,0001	—	0,0014	2,0	0,0018	2,2	0,0022	3,0	0,0046	4,0
East. Sayan Mts.	0,0003	1,0	0,0016	1,9	0,0017	2,0	0,0018	2,5	—	—
Transbaikalia	—	—	—	—	0,0019	2,4	0,0023	3,2	—	--
Khakassiya	—	—	0,0018	2,1	0,0017	2,1	0,0021	2,8	—	—
Tuva	—	—	—	—	0,0016	2,0	0,0018	2,5	0,0040	4,5
Altai Mts.	—	—	—	—	0,0018	2,2	0,0022	2,9	--	—
Tien Shan	—	—	0,0016	2,0	0,0018	2,1	0,0017	2,4	0,0030	3,5
Far East	—	—	—	—	0,0016	1,9	0,0017	2,5	· -	—

Note: Comma represents decimal point.
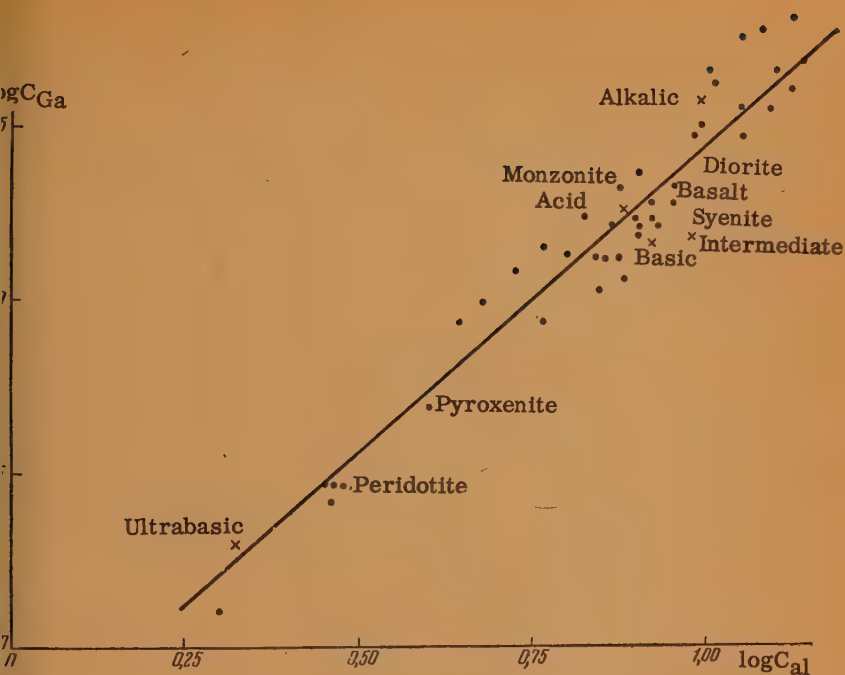
Fig. 1. Concentration of gallium as a function of the aluminum content
in the rock

● -- individual rocks, x - average samples
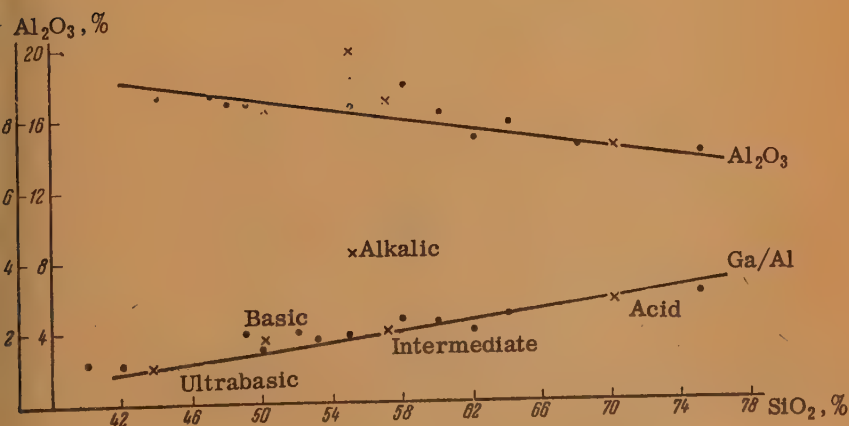
Fig. 2. Variation in the Al_2O_3 content and the Ga/Al ratio with the SiO_2
content in the rock

● -- individual rocks, x - average samples

studied the distribution of gallium and other dispersed elements in the minerals of pegmatites and enclosing rocks of New England.

The results of the present research indicate an approximately tenfold increase in gallium content from the ultrabasic to acid rocks, i.e., from 0.0002% to 0.0020%. The intermediate and basic rocks contain somewhat less gallium than the acid rocks. The increase in the concentration of gallium parallels the increase in the aluminum content in the rocks (Fig. 1). The scatter of points about the straight line representing the logarithm of concentration of gallium as the function of the logarithm of concentration of aluminum is slight. However, if the concentration of gallium in rocks were strictly proportional to the content of aluminum, the Ga/Al ratio would be practically the same for all types of rocks. Actually the ratio increases from the ultrabasic to acid and alkalic rocks. The variation in the Al_2O_3 content and the Ga/Al ratio with the variation in the SiO_2 content is presented in Fig. 2. The SiO_2 content in the rocks is plotted on the axis of the abscissas and the Al_2O_3 content and the Ga/Al ratio on the axis of the ordinates. The diagram shows that the two curves approach each other as the SiO_2 content increases. This illustrates the tendency of the acid rocks, containing a little less Al_2O_3 than the intermediate and basic rocks, toward enrichment in gallium. The accumulation of gallium in the products of final crystallization is confirmed also by its higher content in pegmatites as compared with the minerals of the enclosing rocks. This is especially clearly shown by the alkalic pegmatites (Table 12).

Table 12

Distribution of Gallium Between Minerals
of Pegmatites and Minerals of the Enclosing Rocks

Region	Mineral	Gallium content in rock, %	Gallium content in pegmatite, %	Ga/Al · 10^{-4} in rock	Ga/Al · 10^{-4} in pegmatite
Enisei Range	Nepheline	0.0044	0.0069	2.4	3.6
	Nepheline	0.0047	0.0071	2.5	3.7
	Microcline	0.0024	0.0051	2.6	5.6
	Aegirine	0.0014	0.0024	–	–
Akchatau	Biotite	0.0170	0.0339	24.0	50.0
	Microcline	0.0045	0.0047	4.0	5.3
	Albite	0.0030	0.0050	3.5	5.1
Ukraine	Microcline	0.0019	0.0033	2.1	3.7
	Nepheline	0.0068	0.0098	3.9	6.0
	Biotite	0.0070	0.110	–	–
Alrai Mts.	Microcline	0.0011	0.0012	1.2	1.2

In some cases minerals from pegmatites and from enclosing rocks contain the same amount of gallium (for example, microcline from the Altai

lite and pegmatite and the potassium feldspar from the Enisei Range
natite granite). The preliminary investigations on the distribution of
ium during the differentiation of a single magmatic chamber (as illus-
ed by the Central Kazakhstan massif and the Susamyr batholith of the
a Shan) show a great uniformity both in the absolute content of gallium
in the Ga/Al ratio.

The regional distribution of gallium also shows great uniformity, and it
ears impossible to single out any "gallium provinces." Some regions
enriched in gallium because of the abundance of alkalic rocks and peg-
ites in them and because of postmagmatic alteration of the igneous rocks
casomatism, greisenization). Among such regions are the Kola Penin-
, the Ukraine, the Enisei Range, Transbaikalia and the Altai Mountains.
On the whole, there is an impression of great uniformity in the distribu-
of gallium, whatever the age, locality or conditions of formation of the
cs. This is a manifestation of the intimate connection between gallium
aluminum.

But gallium does not always follow aluminum in its geochemical history.
re are cases in nature when the two elements become separated owing
le slight differences in their properties (different amphoteric properties,
erence in the solubility of their fluorides and complex compounds with
rine, different mobility of their ions, etc.). The difference in the solu-
y of gallium and aluminum fluorides in acid solutions leads to the forma-
of cryolite, an aluminum mineral, which usually does not contain gal-
l. The difference in the amphoteric properties causes the separation of
ium and aluminum in the supergene zone. The author analyzed the hal-
ites of Podmoskov'e (products of weathering of clays) and of the Altai
ntains (products of weathering of granites) and found no gallium. The
ahalloysite of the Zhdanovsk deposit in the Ukraine, derived from neph-
e, contains very small amounts of gallium (0.007%). Evidently gallium
aluminum separate both in acid and in alkaline environments. The au-
· believes that further investigations in the geochemistry of gallium
ild be directed towards the determination of the means by which it be-
es separated from aluminum in the earth's crust.

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ISTRIBUTION OF RUBIDIUM AND LITHIUM
IN ROCKS OF THE LOVOZERO MASSIF

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Rubidium and lithium are geochemical indicators which help to deter-
he the age sequence of igneous rocks in complex intrusions. It is known
t rubidium and lithium become concentrated in the latest acid magmatic
erentiates. For this reason they have aroused considerable interest
ong investigators, and in recent years many data have accumulated in
literature on the content of these elements in igneous rocks.

The published data on the distribution of rubidium and lithium in nephe-
syenites are very scant [1, 2] and are nonexistent for such rocks of
Soviet Union.

Below are the results of our investigation of the distribution of rubidium
lithium in the nepheline syenites of the Lovozero massif (Kola Penin-
a). This massif is a complex intrusive body formed in several stages
is composed of the following rocks (beginning with the oldest):

I -- equigranular, porphyritic, poikilitic and other varieties of nepheline
nites (1st phase);

II -- lujavrites, foyaites, and urtites (2nd phase);

III -- eudialyte lujavrites and associated porphyritic lujavrites, tavites,
kilitic sodalite syenites (3d phase);

IV -- a complex of young dike rocks (4th phase).

The bulk of the massif is composed of the rocks of the second intrusive
se (lujavrites, foyaites, and urtites), forming its lower part and meas-
ng about 900-1000 m in thickness, and of the rocks of the third phase
dialyte lujavrites, etc.), measuring 300-400 m in thickness and forming
upper part.

The rubidium and lithium content in the rocks of the massif is given in
Table.

The content of the alkali metals in the rocks was determined by flame
ctrophotometry using an air-acetylene flame and the double glass mono-
romator DM. The intensity of the spectral lines was measured by the
tomultiplier FEU-22, the anode current being recorded by a mirror
vanometer with the sensitivity of 2.10^{-9} a/mm. The width of the entrance

and exit slits was 0.10 - 0.15 mm for Li, Na and K, and 0.06 - 0.08 mm
for Rb. The following lines were measured: Li -- 670.7 mμ, Na --
588.9 mμ, K -- 766.5 mμ and Rb -- 780.0 mμ.

Analytical procedure. A 500 mg sample of powdered rock was placed in a platinum cup, mois
tened with a few drops of water, and treated with 20-25 ml of hydrofluoric and 1-2 ml of sulfuric
acid. The sample was heated until the appearance of SO_3 fumes. When necessary the treatment
was repeated. The excess of sulfuric acid was removed by heating to 300-350°C. The dried
residue, while being warmed, was dissolved in 10 ml of concentrated hydrochloric acid and trans
ferred into a 50 ml flask. A concentrated solution of aluminum chloride was added to the content
of the flask until its concentration in the flask was not less than 3 mg/ml. The addition of an alu
minum salt is necessary because calcium and strontium present in the sample give strong lines in
the 670 mμ region, which considerably complicate the detection of lithium. Aluminum forms com
pounds of the $\underline{x}$ $Al_2O_3 \cdot \underline{y}$ CaO (SrO) type with calcium and strontium, which have a high melting
point, and thus the intensity of lines interfering with lithium analysis is considerably lowered.

The Content of Alkali Metals in the Rocks of the Lovozero Massif

Sample No.	Locality	Name of rock	Content, %				
			Na$_2$O	K$_2$O	Li$_2$O	Rb$_2$O	K/Rb
Rocks of the first complex (miaskitic)							
183	Alluaiv Mt.	Porphyritic nepheline syenite	10.75	5.2	0.0068	0.014	337.
296	Alluaiv Mt.	Poikilitic nepheline syenite with hydrosodalite	11.3	4.8	0.0030	0.011	396.0
139	Ninchurt Mt.	Equigranular biotite nephe-line syenite	10.9	3.5	0.0035	0.011	288.4
66	Suoluaiv Mt.	Poikilitic nepheline syenite	11.4	4.3	0.014	0.015	229.3
Rocks of the second complex (agpaitic)							
146	Karnasurt Mt.	Ijolite–urtite with apatite	16.0	3.6	0.0035	0.022	148.
187	Alluaiv Mt.	Ijolite–urtite	15.4	4.4	0.0055	0.029	137.
143	Karnasurt Mt.	Foyaite	8.6	6.9	0.0043	0.040	149.
144	Karnasurt Mt.	Foyaite	9.6	6.15	0.0035	0.037	150.7
38	Alluaiv Mt.	Trachytoidal foyaite	10.3	4.5	0.0040	0.0095	429.4
362	Parguaiv Mt.	Leucocratic lujavrite	12.40	4.60	0.0069	0.020	208.5
162/35	Kuftn'yun Mt.	Leucocratic lujavrite	9.1	6.30	0.0075	0.0395	146.4

Table (Continued)

The Content of Alkali Metals in the Rocks
of the Lovozero Massif

Sample No.	Locality	Name of rock	Content, %				
			Na_2O	K_2O	Li_2O	Rb_2O	K/Rb
0	Karnasurt Mt.	Leucocratic lujavrite	11.0	5.17	0.0105	0.0285	164.5
4	Alluaiv Mt.	Melanocratic lujavrite	9.2	4.40	0.0082	0.025	159.6
3	Karnasurt Mt.	Melanocratic lujavrite	9.5	5.0	0.0053	0.029	156.3
5	Karnasurt Mt.	Mesocratic lujavrite	8.5	5.8	0.0043	0.036	146
3	Karnasurt Mt.	Amphibole lujavrite	9.3	4.70	0.0260	0.016	259.5
4	Alluaiv Mt.	Lujavrite with loparite	8.8	4.70	0.0050	0.026	164
2	Alluaiv Mt.	Urtite with loparite	10.1	3.0	0.0050	0.012	226.6
3	Alluaiv Mt.	Urtite with apatite and loparite	6.1	1.0	0.0004	0.0014	647.6
67	Karnasurt Mt.	Malignite with loparite	10.3	2.8	0.0040	0.016	158.6

Rocks of the third complex (agpaitic)

5	Alluaiv Mt.	Eudialyte lujavrite	9.75	4.85	0.0275	0.035	125.6
0	Alluaiv Mt.	Eudialyte lujavrite	10.00	4.85	0.0063	0.045	97.7
6	Alluaiv Mt.	Porphyritic juvite with loparite	12.7	4.8	0.0038	0.029	150.0
3	Karnasurt Mt.	Porphyritic lovozerite lujavrite	8.0	4.45	0.0200	0.040	110.9
6	Vavnbed Mt.	Porphyritic lovozerite lujavrite with lomonosovite	8.2	4.60	0.0320	0.035	119.2
XI	Flora Mt.	Porphyritic lujavrite with murmanite	10.0	5.1	0.0060	0.041	112.8
1	Chinglusuai Mt.	Poikilitic sodalite syenite	13.0	3.4	0.0047	0.0091	338.8

Table (Continued)

The Content of Alkali Metals in the Rocks of the Lovozero Massif

Sample No.	Locality	Name of rock	Content, %				
			Na_2O	K_2O	Li_2O	Rb_2O	K/Rb
430	Source of the Tavaiok River	Tawite	13.2	1.4	0.0044	0.0045	282.0
266	Valley of the Tulbn'yunuai River	Poikilitic sodalite syenite	14.5	3.8	0.0175	0.009	382.8

To determine sodium and potassium, an aliquot portion of the solution was taken out of the 40 ml flask and diluted so as to keep the concentration of Na and K between 5 and 40 μ/ml. The standard solutions contained the same amounts of hydrochloric acid and aluminum as in the samples. The ratio of the concentration of K and Na in the solutions was also approximately the same as in the rocks. To determine lithium and rubidium, standard solutions were prepared with added sodium and potassium in amounts approximately corresponding to the content of these elements in the sample. They could be used for both lithium and rubidium analysis. The standard solutions for photometry contained: 0.0, 0.1, 0.2, 0.5, 1.25, 5.0, 10 γ/ml lithium and 0.0, 0.2, 0.5, 1.0, 2.0, 5.0, 10 and 20 γ/ml rubidium. In the photometry of the samples, the background was measured on either side of the lines, while for the standards, the intensity of the zero solution was measured. The average values of the background were subtracted from the intensity of the lines and the concentration of lithium and rubidium was determined graphically. Samples containing less than 0.01% Rb and less than 0.001% Li were analyzed by the method of addition. Exact solutions were prepared by dissolving the dry chlorides in distilled water.

The data presented in the Table show that the rubidium and lithium content in the rocks of the massif varies within broad limits from 0.0014% to 0.045% Rb_2O and from 0.0004 to 0.047% Li_2O.

There is no direct relation between the content of rubidium and potassium, although it should be noted that the minimum amounts of rubidium (0.0014% and 0.0045% Rb_2O) were found in rocks very poor in potassium (1.0% to 1.4% K_2O, respectively). The potassium–rubidium ratio varies from 97.7 to 647.6 (see table), and its average for the massif is about 220. The value of this ratio is higher than in acid rocks (83.5) and lower than in intermediate rocks (370).

The average rubidium content in the rocks of the first complex is 0.01, of the second, 0.026 and of the third, 0.039% Rb_2O. If it is considered that the rocks of the first complex constitute probably no more than 1% of the total volume of the massif, the rocks of the second complex about 75% and of the third, about 24%, the total rubidium content in the massif is about 0.029% Rb_2O (0.026% Rb). This content is somewhat lower than the value for nepheline syenites (0.044% Rb_2O) given in the literature[1, 2].

The data show that rubidium accumulates during the evolution of the magma. The rocks of the third phase are richer in rubidium than those of the first and second phases. The sodalite-bearing rocks genetically related to the rocks of the third phase form an exception. They contain little

bidium. This is probably due to their low potassium content.

The distribution of lithium in the rocks of the massif is very irregular, specially in the rocks of the second intrusive phase (from 0.0004 to 0260% Li_2O).

The maximum amount of lithium was found in the amphibole lujavrite .0260% Li_2O). This rock contains much magnesium-bearing alkalic amibole. According to O.A. Vorob'eva (oral communication) the alkalic aphibole (arfvedsonite) from the amphibole lujavrite contains 9.32% MgO .A. Moleva, analyst). It should be noted that Fersman [3] suggested that hium may become concentrated in the lattices of ferromagnesian minerals the substitution of Al + Li for magnesium.

The average lithium content in the rocks of the first phase is 0.0068%, the second, 0.0052%, of the third, 0.0167% Li_2O, and for the massif as a ole, probably 0.0079% Li_2O (0.0037% Li). It is higher than the published lue of nepheline syenites (0.00235% Li) [1, 2].

The rocks of the third phase contain considerably more lithium than the cks of the first and second phases, indicating accumulation of lithium wards the end of the magmatic evolution of the massif.

The relatively high lithium content in the rocks of the Lovozero massif s unexpected. Opinion existed that lithium is not a characteristic ele- ent of nepheline syenites. This opinion is reflected in the literature. rsman [3], in his geochemical analysis of the Khibina and Lovozero calic massifs, based on the very scant data on the distribution of lithium nerals then available, wrote, "The almost complete absence of lithium in e alkalic plutons, except for minute flakes of taeniolite, is characteristic."

The Rb/Li ratio for the Lovozero massif as a whole is 7.0. For individ- l rock types it varies, within broad limits, from 20.8 to 0.1. The lowest lues of the Rb/Li ratio characterize a number of rocks of the third com- ex, the poikilitic sodalite syenite (0.1), tawite (2.0), the eudialyte luja- ite (1.6–2.5) and the porphyritic lovozerite lujavrite (2.1), and also the nphibole lujavrite from the second complex (1.2). All these rocks are nsiderably enriched in lithium. The highest values of the Rb/Li ratio).8 and 18.3) are characteristic of foyaites, rocks with high content of bidium (0.037% and 0.040% Rb_2O) and potassium (6.15% and 6.9% K_2O).

The preliminary investigations of the distribution of rubidium and lithium the nepheline syenites of the Lovozero massif show that:

2) lithium and rubidium are very irregularly distributed in the rocks of e massif, due mainly to the very variable composition of the rocks;

b) there is no direct relation between the content of rubidium and potas- im and between the content of lithium and magnesium;

c) the accumulation of rubidium and lithium occurs at the end of the agmatic process (in the rocks of the third intrusive phase);

d) lithium is a characteristic element in the Lovozero massif.

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THE OCCURRENCE OF SCANDIUM AND SOME OTHER RARE ELEMENTS IN CASSITERITE

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The presence of scandium in cassiterite was first established by G. Eberhard in 1908 [1]. However, the form of occurrence of scandium in cassiterite is still unknown.

V.M. Goldschmidt [2, 3] suggested that scandium enters into tin-stone in the form of $ScNbO_4$. But although this hypothesis has since been reiterated by a number of investigators, the presence of $ScNbO_4$ in the structure of cassiterite remains unproved.

Although the data presented in our work are not exhaustive, we believe that they do give an idea as to the form in which scandium enters into the structure of cassiterite.

We have investigated cassiterite from 52 different localities in the Soviet Union and from 22 foreign localities (altogether, more than 300 specimens were analyzed). Spectrography was used as the basic method for the determination of scandium and niobium in the minerals. The sensitivity of determination of scandium and niobium was 0.001% of the metal. The precision of the determinations was ± 10%.

The results of the investigation showed that all scandium-bearing cassiterites contain niobium. On the other hand, as in the case of wolframites [4], we found that not all niobium-bearing cassiterites necessarily contain scandium. T

Table 1

Distribution of Scandium
and Niobium in Cassiterites
of the Rare Metals Deposits
of the Soviet Union

Sc	Nb	Number of samples	Number of deposits
+	+	101	15
+	–	–	–
–	+	66	20
–	–	106	17

+ present

– absent

ata are given in Tables 1, 2 and 3.

Table 1, which gives the distribution of scandium and niobium in the assiterites from the Soviet Union localities, shows that 1) cassiterites rom 15 localities (29% of all investigated cassiterites) contain both scandim and niobium; 2) cassiterites from 20 localities (38.5%) contain niobium nly; and 3) cassiterites from 17 localities (32.5%) contain neither scandim nor niobium.

Table 2, which lists scandium and niobium content in the cassiterites rom some of the foreign localities, also shows that scandium is absent rom many niobium-bearing cassiterites.

Table 2

Scandium and Niobium Content in Cassiterites
From Some Foreign Deposits

Locality	Type of deposit	Number of analyses	Content in %	
			Sc_2O_3	Nb_2O_3
Erongo, South-West Africa	Pegmatite	2	–	1.19
Poqueb, South-West Africa	"	3	–	0.91
Wudinna, Australia	"	2	–	1.33
Zinnwald, Germany	Pneumatolytic-hydrothermal	2	0.049	1.3
Czechoslovakia	"	3	0.17	1.08
Southern Thailand	Hydrothermal	2	–	0.57
Luigi River, Malacca	"	2	–	0.014
Graupen, Czechoslovakia	"	2	–	–
Ehrenfiedersdorf, Germany	"	2	–	–
Andreasburg, Germany	"	2	–	–
Altenberg, Germany	"	2	–	–
Totora and other districts, Bolivia	"	6	–	–

From Table 3, we see clearly that the high niobium content is not the aain factor determining the presence of scandium. The cassiterites from ranite pegmatites which contain maximum amounts of niobium, 3.4% Jb$_2$O$_5$ (group A deposits: Bel'sk, Eastern Sayan Mts.; Ak Kezen', Kalba; Jaukinskoe, Turkestan, and others), do not, as a rule, contain scandium. On the other hand, scandium is frequently present in the high temperature neumatolytic-hydrothermal deposits of the greisen type (group B deposits: Etyka, Eastern Transbaikalia; Polyarnoe, Northeastern Asia; Zinnwald, Erz Mountains). It should be stressed that the average niobium content in he cassiterites of the pneumatolytic-hydrothermal deposits is generally 4 o 5 times lower than in the pegmatitic cassiterites. An exception are the Etyka cassiterites, in which the Nb_2O_5 content reaches two and more percent. The high niobium content in the pegmatitic cassiterites as compared vith the cassiterites of hydrothermal origin was noted by Ya. Larionov and Yu. V. Tolmachev[5], S.A. Borovik and Ya. D. Gotman[6], A.M. Boldyreva[7]

Table 3

Average Sc_2O_3 and Nb_2O_5 Content in Cassiterites of the Rare Metals Deposits of Different Origin in the USSR

Type of deposit	Locality, region	Number of analyses	Average content in %	
			Sc_2O_3	Nb_2O_5
1	2	3	4	5
A In pegmatites	Urikskoe (Eastern Sayan Mts)	2	0.035	0.73
	Bel'skoe (Eastern Sayan Mts)	12	none	1.62
	Gol'tsovskoe (Eastern Sayan Mts)	1	"	1.50
	Belorechenskoe (E. Sayan Mts)	2	"	0.72
	Naukinskoe (Uzbekistan)	5	"	1.90
	Samzhon (Turkestan Range)	2	"	1.96
	Ak Kezen' (Kalba)	5	"	2.38
	Karmen Kuus (Kalba)	2	"	1.68
	Azvitinskoe (Eastern Transbaikalia)	2	"	1.54
	Malo–Kulindinskoe (E. Transbaikalia)	2	"	1.61
B Pneumatolytic–hydrothermal (greisen)	Polyarnoe (Yakutia)	32	0.075	0.47
	Etyka (Eastern Transbaikalia)	30	0.066	2.17
	Kara–Oba (Central Kazakhstan)	14	0.011	0.46
	Kara–Oba (Central Kazakhstan)	6	none	0.41
C Hydrothermal a) quartz–cassiterite	Privalovsoe (Eastern Transbaikalia	3	0.025	0.94
	Uval'noe (Eastern Transbaikalia)	4	0.008	0.24
	Lokermanovskoe (E. Transbaikalia)	2	0.005	0.06
	Imalkinskoe (E. Transbaikalia)	5	0.006	0.04
	Sokhondo (E. Transbaikalia)	2	0.005	0.28
	Dedova Gora (E. Transbaikalia)	4	none	0.22
	Aldakachan (E. Transbaikalia)	3	"	0.09

Table 3 (Cont'd.)

Average Sc_2O_3 and Nb_2O_5 Content in Cassiterites
of the Rare Metals Deposits of Different Origin in the USSR

Type of deposit	Locality, region	Number of analyses	Average content in %	
			Sc_2O_3	Nb_2O_5
1	2	3	4	5
sulfide-cassiterite deposits	Sherlova Gora (E. Transbaikalia)	2	0.012	0.06
	Sherlova Gora (E. Transbaikalia)	1	none	0.01
	Deputatskoe (Yakutia)	28	"	none
	Illintas (Yakutia)	5	"	"
	Ege-Khaya (Yakutia)	8	"	"
	Lifudzinskoe (Primor'e)	21	"	"
	Khrustal'noe (Primor'e)	15	"	"
	Verkhne-Kentsukhinskoe (Primor'e)	27	"	"

others. Most of the earlier works, however, gave only qualitative esti-
tes of the content of rare elements in cassiterites.

In the cassiterites of some hydrothermal deposits of the quartz-cassi-
ite type, small amounts of scandium are occasionally present (group C
osits: Privalovskoe, Uval'noe, Lokermanovskoe, and Sokhondo, all in
stern Transbaikalia). The average niobium content in most cassiterites
m the deposits of this group is lower than in the cassiterites from peg-
tites and greisen.

Finally, the majority of the analyzed specimens from sulfide-cassiterite
osits contain neither niobium nor scandium (Deputatskoe deposit, Lifu-
inskoe, Khrustal'noe, etc.).

These data on the character of the distribution of scandium and niobium
cassiterites from deposits of different genetic types show that scandium
not a constant companion of niobium. It is either absent or present only
insignificant amounts in pegmatite and hydrothermal deposits, and ac-
mulates in considerable amounts only in the cassiterites from high tem-
rature pneumatolytic-hydrothermal deposits. In the cassiterites from
ese deposits there is, however, no clear correspondence between the con-
nt of scandium and niobium. It is enough to consider the Polyarnoe de-
sit as an example to be convinced of this. The curves of variation of
$_2O_3$ and Nb_2O_5 content constructed for ten specimens of cassiterite from
is deposit (see diagram) show that although there is a general tendency
r scandium and niobium (left to right) to diminish together, there is no
rect linear relationship between the variations in the Sc_2O_3 and Nb_2O_5
ntents.

Another example pointing to the absence of direct relation between the
andium and niobium content in cassiterites is furnished by the data of

Table 3, columns 4 and 5. The cassiterites from the Polyarnoe deposit (Yakutia) contain 0.47% Nb_2O_5 and 0.075% Sc_2O_3, while the cassiterites from the Etyka deposit (Eastern Transbaikalia) contain 2.17% Nb_2O_5 and 0.066% Sc_2O_3.

Our investigations of cassiterites of different origin confirm the data of I. F. Grigor'ev and E. I. Dolomanova [8] on the presence of tungsten in all cassiterites of pneumatolytic-hydrothermal type. Tungsten is usually absent from the cassiterites of pegmatite and sulfide-cassiterite deposits; i.e., it is absent from those cassiterites which are also devoid of scandium. We analyzed ten cassiterites from the pegmatites of the USSR and only in the specimens from the Urikskoe deposit were both scandium and tungsten found. In the rest of the pegmatitic cassiterites, these elements were absent. The association of tungsten and scandium in the cassiterites of pneumatolytic-hydrothermal deposits suggests an affinity of scandium for tungsten rather than for niobium.
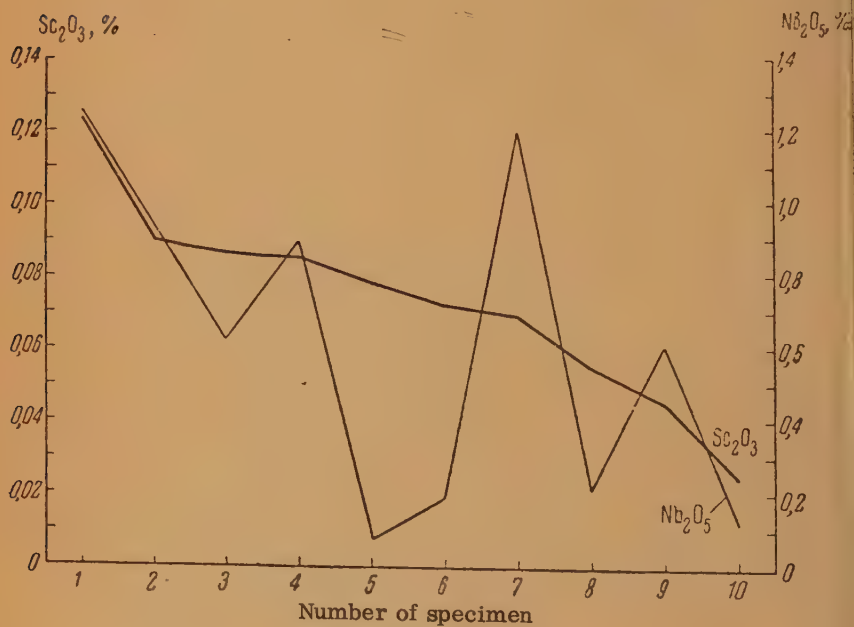
Scandium and niobium content in cassiterites

However, our calculations for the cassiterite from the Etyka deposit show that a direct chemical affinity between scandium and tungsten is improbable. In 1951, Grigor'ev and Dolomanova [8] showed that niobium and tungsten may be present in cassiterite in the form of minute mechanical inclusions of columbite and wolframite. By a simple recalculation of the results of chemical and spectroscopic (qualitative) analyses of cassiterite, it

is easy to show that not all of the scandium can be present in the inclusions of columbite and wolframite. The analysis of the Etyka cassiterite (Eastern Transbaikalia) gives 2.7% of columbite and 0.8% of wolframite (assigning all of the Nb_2O_5 and WO_3 in the cassiterite to these two minerals). The average Sc_2O_3 content in the cassiterite from this deposit is 0.066%, and in the wolframite it is about 0.05%. The analyses of columbites show that their Sc_2O_3 content is usually not over 0.05%. It follows that the wolframite inclusions in the Etyka cassiterite may contain about 0.0004% Sc_2O_3 and those of wolframite, about 0.0013%, i.e., about 0.017% Sc_2O_3 altogether, an amount which constitutes only 3% of the average Sc_2O_3 content in the Etyka cassiterite (0.066%). Thus, there must be some other way in which scandium enters into the composition of cassiterite. It appears possible that scandium ions (r_i = 0.83 A) may diadochically replace tin ions (r_i = 0.67 A) in the structure of cassiterite. The charges may be balanced by the simultaneous substitution of a part of the tin ions (Sn^{4+}) by niobium ions (Nb^{5+}) according to the equation, $2Sn^{4+} \leftarrow Sc^{3+} + Nb^{5+}$. The sixfold coordination of these elements (Sc, Nb, Sn) in natural compounds favors this kind of substitution. The diadochy between scandium and niobium and tin is by no means contradicted by the occurrence of mechanical inclusions of columbite (and wolframite) in cassiterite, because the balancing of charges requires only a very small amount of niobium.

Besides scandium, niobium and tungsten, many of the analyzed specimens of cassiterite contain tantalum, and all of them contain zirconium. Evidently tantalum plays a role analogous to that of niobium. Zirconium is probably present in cassiterite in the form of microscopic inclusions of a zirconium mineral, as has already been noted by Grigor'ev and Dolomanova [8].

Summary

1. Scandium occurs in considerable amounts (up to 0.2% Sc_2O_3), mainly in the cassiterites from pneumatolytic-hydrothermal deposits of the greisen type, and is almost never found in cassiterites from pegmatites and sulfide-cassiterite deposits.

2. All scandium-bearing cassiterites contain niobium (up to 2-3% Nb_2O_5), tungsten and zirconium, and many of them contain tantalum (hundredths and tenths of one percent). However, not all niobium-bearing cassiterites contain scandium. The presence of niobium in cassiterites does not necessarily indicate the presence of scandium. Especially noteworthy in this respect are the pegmatitic cassiterites.

3. It is most probable that scandium (Sc^{3+}) enters into cassiterite by diadochically replacing tin ions (Sn^{4+}). The charge is balanced by the substitution of a part of the tin ions by niobium ions (Nb^{5+}).

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ON THE EXISTENCE OF ISOTOPE SHIFTS
IN NATURAL THORIUM COMPOUNDS

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A number of recently published papers [1, 2, 3] discuss the possibility of change in the isotopic composition of thorium in its natural compounds. The hypothesis of isotope shifts between Th^{228} and Th^{232} is based on the fact that Th^{228} forms from Th^{232} as a result of radioactive decay according to the scheme:

$$Th^{232} \xrightarrow[1,4 \cdot 10^{10} \text{ l yr.}]{\alpha} Ra^{228}(MsTh_1) \xrightarrow[6,7 \text{ l yr.}]{\beta} Ac^{228}(MsTh_2) \xrightarrow[6,1 \text{ l yr.}]{\beta}$$

$$Th^{228}(RdTh) \xrightarrow[1,9 \text{ l yr.}]{\alpha} .$$
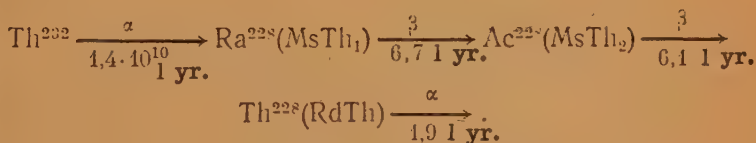
Therefore, the removal of the intermediate products of decay, and particularly of Ra^{228}, and, by analogy with uranium [1, 4], the possible variation in the position of thorium isotopes in minerals causing them to be more or less easily leached will result in isotope shifts.

It is believed that the magnitude of these shifts in thorium minerals is slight, first, because natural thorium compounds are rather stable, as shown by the scarcity of secondary thorium minerals, and, second, because the time required for the re-establishment of the isotopic composition in thorium is short (of the order of a few decades).

The object of the present work was an investigation of the behavior of different thorium isotopes in minerals. Specimens of thorium minerals used in the investigation were donated by A.I. Polyakov. As it was expected that the isotope shifts in thorium would be small, the determination of its isotopic composition was made by the direct method based on

simultaneous and independent determination of the content of each isotope by means of the apparatus used in measuring alpha-spectra.

Preparation of Thorium-Bearing Minerals

Leaching. The weighed sample (thorite or monazite with 0.1-0.25 mm particle size) was leached by 0.2N HCl for ten days, and the solution was filtered off and used for the determination of the isotopic composition of thorium (for thorite, the treatment was repeated). The isotopic composition of thorium remaining in the residue after leaching was also determined.

Separation of thorium. To determine the isotopic composition of thorium by alpha-particle spectrometry, it is necessary to have thorium of sufficient radiochemical purity. Alpha-spectrometric analysis is interfered with by the elements whose isotopes emit alpha-particles with energies comparable to those of the alpha particles of thorium isotopes, i.e., by the isotopes of uranium, radium and polonium. Moreover, to obtain sufficiently thin layer of thorium suitable for the alpha-particle spectrometric study by electrodeposition, it is necessary first to separate thorium from the elements which are deposited with it, such as iron and zirconium.

After the thorium-bearing mineral was decomposed, 10 mg of zirconium (in the form of nitrate) was added to the solution to serve as carrier for trace amounts of thorium, and the zirconium (thorium) iodates were precipitated from the nitric acid solution in the presence of hydrogen peroxide. The iodates were reprecipitated under the same conditions and decomposed with hydrochloric acid containing hydroxylamine hydrochloride. The solution was evaporated to dryness, the residue dissolved in 8 $\underline{N}$ HCl and the solution passed through a column containing anionite EDE-$\overline{10}$ P to separate iron, traces of uranium, polonium and, in part, bismuth [5, 6]. Zirconium (thorium) hydroxides were then precipitated from solution; the precipitate was filtered off, dissolved in a mixture of nitric and hydrochloric acid and evaporated to dryness. The residue was dissolved in 2 $\underline{N}$ HCl and the solution was passed repeatedly through the ion exchange column to eliminate traces of polonium and bismuth. After this, the solution was passed through a column with cationite KU-2 and then zirconium was leached out with 0.5% solution of oxalic acid and thorium, with 3 $\underline{N}$ H_2SO_4 [7, 8]. The sulfuric acid solution was evaporated to dryness and the residue was used in the electrolysis.

Electrolytic deposition of thorium. For the determination of the isotopic composition by alpha-particle spectrometry, it is necessary to have thin strong homogeneous films of thorium. Electrodeposited films are most convenient for this purpose. For the investigation of the isotopic composition of thorium, quantitative separation of thorium during the electrolysis is not necessary, but the most complete separation and utilization of small amounts of thorium are desirable. The methods of electrodeposition of thorium formerly used did not quite fulfill these requirements. The electrolysis of weakly acid solutions of thorium and zirconium gives incoherent precipitates [9]; in the electrolysis of solutions containing thorium nitrate and potassium ferrocyanide, a large amount ($\sim$100 mg) of thorium is required, and a platinum cathode must be used [10], and the electrolysis of thorium salts dissolved in alcohol or in a mixture of alcohol and acetone [9] also requires large amounts of thorium ($\sim$ 3-5 mg/ml).

We tried electrodeposition of thorium from a solution in alcohol and

acetone (4:1) at room temperature. The results showed that this method can be used with 5-50 mg of thorium, using current density of 2-3 ma/cm^2 and continuing the electrolysis for 15-30 sec. If the electrolysis is continued longer, a loose deposit is obtained. A loose deposit was obtained by this method in the attempt at electrodeposition of small amounts of thorium in the presence of zirconium.

A method analogous to that proposed for electrodeposition of small amounts of uranium [11] was used in the present work. It is very convenient for amounts of thorium from 0.1 to 1.0 mg, and gives good dense sufficiently homogeneous films quite suitable for alpha-particle spectrometric determination of the isotopic composition of thorium.

For the electrodeposition, the thorium salt was dissolved in 15 ml of water to which were added, one after the other, 5 ml of 4% solution of ammonium oxalate, one drop of methyl red, a few drops of 6 $\underline{N}$ HCl (the solution turns yellow) and a few drops of 6 $\underline{N}$ HNO$_3$ (the solution turns red). The electrolysis was conducted at 80°C and with stirring and the cathode current density of 100-150 ma/cm^2. During the electrolysis, a few drops of 6 $\underline{N}$ HNO$_3$ were added periodically to the solution. After 15 minutes, 0.5 ml of 6 $\underline{N}$ NH$_4$OH was added to the solution and the electrolysis continued for 10 minutes more. The total time of electrolysis was 25 minutes. A spiral of platinum wire was used as the anode and stainless steel discs 40 mm in diameter as the cathode.

Under these conditions, 80 to 90% of the thorium is deposited; and without a carrier, 50-60% of the ionium. These amounts may be increased by prolonging the electrolysis. Iron and zirconium are deposited with thorium, as well as 80 to 90% of uranium and considerable amounts of polonium, 80 to 85% of bismuth (Bi^{212}) and 40 to 50% of radium (Ra^{224}).

Instrumentation and Method of Investigation
of the Isotopic Composition of Thorium

The isotopic composition of thorium was investigated by means of a 50-channel apparatus used for measurement of alpha-spectra described in our work [4] on the isotopic composition of uranium.

The apparatus consists of an ionization chamber, preamplifier, linear amplifier with an expander and a differential pulse analyzer. To obtain greater resolution, we used a grid chamber working on the principle of electron collection instead of the previously described chamber with a spherical electrode.

The general view of the ionization chamber is given in Fig. 1 and its main parts are shown diagrammatically in Fig. 2. The chamber is made of metal and consists of a flat horizontal plate supporting a steel dome. The plate rests on four posts which fasten it to the base.

The upper part of the dome contains the collecting electrode, a disc 110 mm in diameter. The collecting electrode is connected through a vacuum lead with the grid of the first tube of the preamplifier which is located directly on the chamber and is grounded through a high value resistor placed within the chamber. To obtain a more uniform electric field, the collecting electrode is shielded by a guard ring. The grid-carrying ring is located beneath the collecting electrode. The outside and inside diameters of the ring are 160 and 140 mm, respectively. Two tungsten wires, 0.05 mm in diameter, are stretched parallel to each other within the grid ring. A high
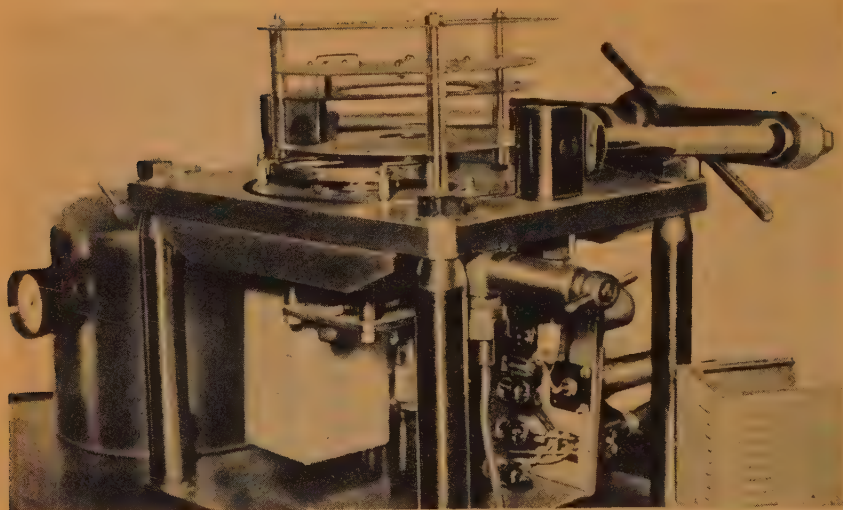
Fig. 1.   General view of grid ionization chamber

voltage disc electrode 160 mm in diameter with a central hole for mounting alpha-active preparations is located beneath the grid. The lower part of the apparatus contains high voltage vacuum leads and the mechanism for changing samples, which allows successive measurement of five samples without recharging the chamber.

The pulses from the collecting electrode pass to the preamplifier mounted under the base of the chamber. The preamplifier has four 6Zh1P tubes and is of the triode amplifier type with feedback and a cathode follower at the output. Its amplification factor is about 100.

From the preamplifier the pulses pass to the main amplifier which has an amplification factor of $\sim 10^4$ and consists of two triodes with negative feedback, discriminator and an additional amplification stage. The pulses of the spectrum amplified to several tens of volts are analyzed by the 50-channel differential pulse analyzer. The spectrum registered by the analyzer appears directly on the tube and can be photographed. The resolution of the apparatus is ~ 45 Kev with the alpha particles energy of ~ 5 Mev.

Fig. 3 shows the alpha spectra of thorium obtained with the apparatus and the system of their recording.

Discussion of Results

The obtained ratios of the thorium isotopes are given in Table 1. The data show that the isotopic composition of thorium in minerals may change. In most investigated minerals the isotopic composition corresponding to or near equilibrium is preserved (samples 3, 4, 6, 8, 9). In some cases there is a noticeable impoverishment of the minerals (karnasurtite,
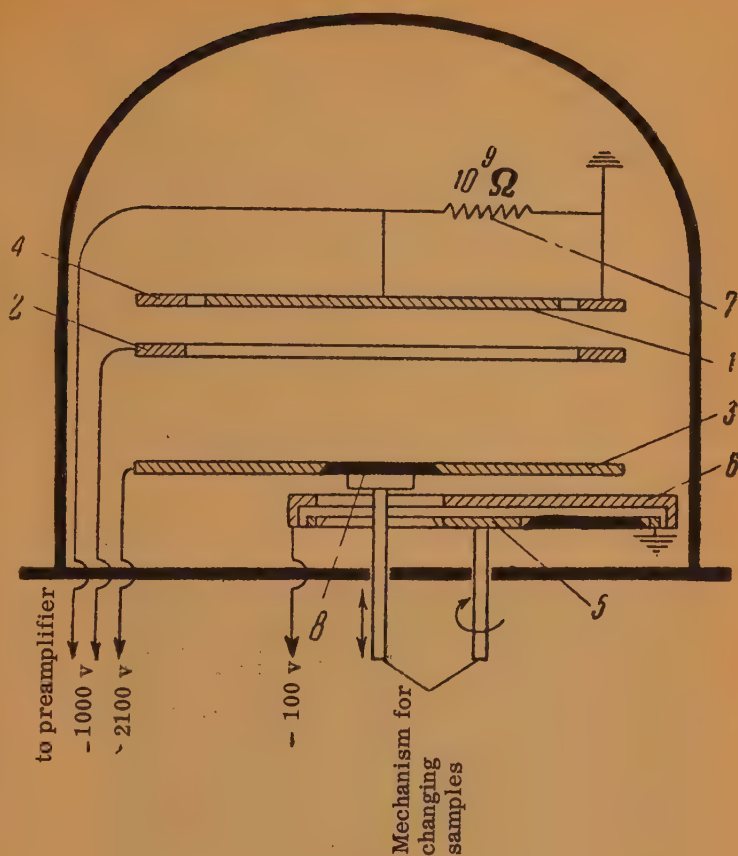
Fig. 2. Main parts of the grid ionization chamber

1 - collecting electrode, 2 - ring with grid, 3 - high voltage
electrode, 4 - guard ring, 5 - sample holder, 6 - sample
holder case, 7 - high value resistor, 8 - sample under
investigation

teenstrupine) in Th^{228} (samples 5, 7) which may be due to the leaching of
Ra^{228} or Th^{228} by ground waters.

Experiments in leaching (Table 2) show that the change in the isotopic
composition depends on the mineral subjected to leaching. For monazite
sample 1) the change is not so great as for thorite (sample 2) leached
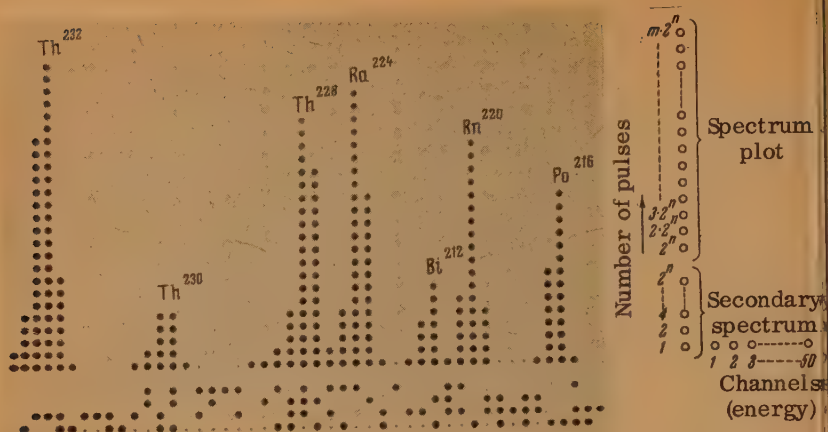
$\underline{a}$
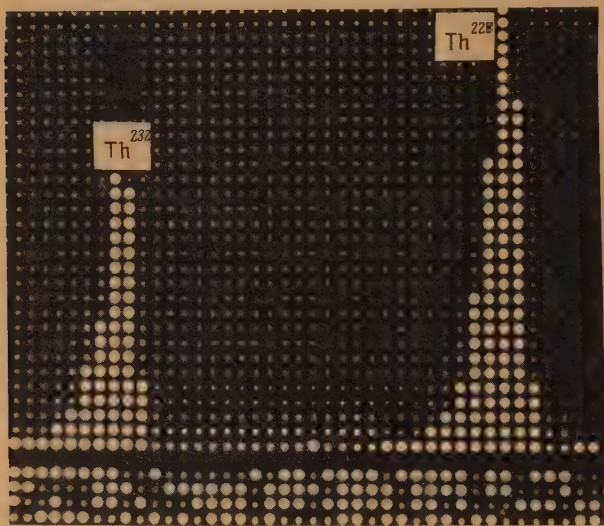
$\underline{b}$

under the same conditions, in which the change in isotopic composition is due mainly to the leaching out of Th^{228}. This may be explained by the different position of Th^{232} and Th^{228} in the mineral. It should be noted that the thorium isotope Th^{230} from the uranium series is leached out to a greater extent than Th^{232}. The experimental data show, therefore, that the isotopic composition of thorium in minerals may change. The method
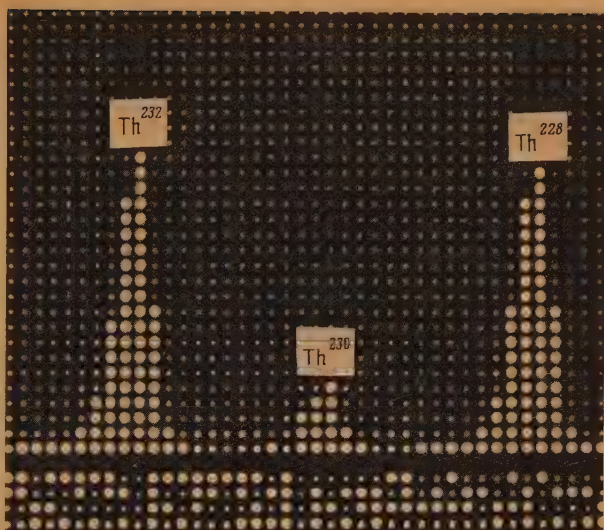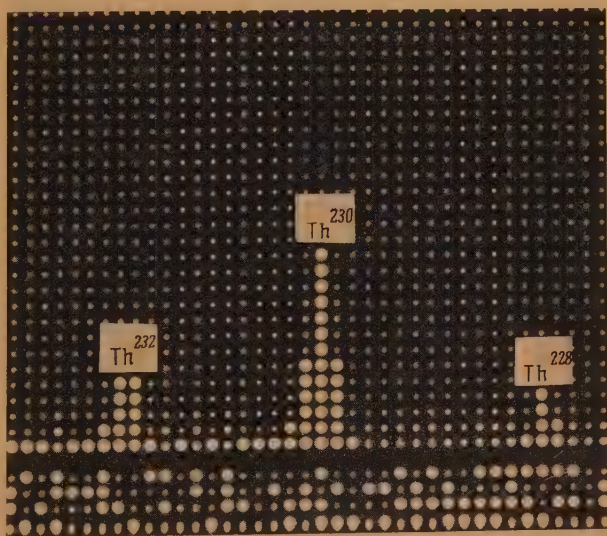
Fig. 3. Alpha spectra of thorium samples
and the system of recording of spectra:

a) spectrum of thorium isotopes and of the products
of decay of Th^{232} and the system of recording of
alpha spectra, b) spectrum of isotopes of thorium
enriched in Th^{228}, c) spectrum of isotopes of
thorium in equilibrium, d) spectrum of isotopes of
thorium impoverished in Th^{228}

Table 1

Isotopic Composition of Thorium in Minerals

No.	Sample	Th^{228}/Th^{232}	Th^{230}/Th^{232}	Th/U (computed)
		in decay products	in decay products	
1	Thorium nitrate (in equilibrium)	0.97 ± 0.02	0.24 ± 0.02	
2	Thorium nitrate	0.29 ± 0.01	0.17 ± 0.01	
3	Thorite	1.03 ± 0.02	0.09 ± 0.01	35.7 ± 1.7
4	Loparite	0.96 ± 0.02	0.18 ± 0.01	17.2 ± 1.0
5	Karnasurtite	0.87 ± 0.01	0.18 ± 0.01	17.2 ± 1.0
6	Lovchorrite	0.92 ± 0.01	0.13 ± 0.01	23.8 ± 1.8
7	Steenstrupine	0.73 ± 0.02	1.74 ± 0.04	1.80 ± 0.05
8	"	0.94 ± 0.01	0.35 ± 0.01	9.1 ± 0.03
9	"	0.94 ± 0.02	0.26 ± 0.01	11.9 ± 0.5
10	Pitchblende		>300	<0.01

Table 2

Isotopic Composition of Thorium
in the Products of Leaching

Sample	Th^{228}/Th^{232}	Th^{230}/Th^{232}
	in decay products	in decay products
Thorite		
1st leaching	1.68 ± 0.02	0.11 ± 0.01
2nd leaching	0.83 ± 0.02	0.06 ± 0.01
residue	0.52 ± 0.01	0.07 ± 0.01
Monazite		
1st leaching	0.94 ± 0.03	0.20 ± 0.03
residue	0.76 ± 0.03	0.20 ± 0.01

of direct determination of the isotopic composition of thorium used in the present work gives very precise Th^{228}/Th^{232} and Th^{230}/Th^{232} ratios and can be used, therefore, for the determination of the Th/U ratio in equilibrium samples by analysis for the isotopic composition of thorium. The observed significant deviations from the equilibrium ratios show that isotope shifts in thorium as well as uranium minerals may be widespread. This effect must be taken into consideration in radiometric determination of uranium and thorium, and also in measurements of the absolute geological age.

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THE ISOTOPIC COMPOSITION
OF LEAD FROM CERTAIN DEPOSITS
OF CENTRAL KAZAKHSTAN

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About forty determinations of the isotopic composition of lead from different deposits of Central Kazakhstan have been published [1, 2]. All of them were made on galena from polymetallic or lead deposits and occurrences of different types and, in one case, on galena separated from rock.

In our opinion, the close similarity of the isotopic composition of lead from the typically hydrothermal deposits and lead from deposits and occurrences which are considered sedimentary by some investigators indicates genetic unity of these leads and their common hydrothermal origin [3].

Although the data on the isotopic composition of lead are fairly extensive, they do not by any means cover all polymetallic and lead deposits, and, moreover, data on the isotopic composition of lead from other types of deposits, such as deposits of rare metals and manganese, are lacking.

The present paper reports the results of investigation of the isotopic composition of lead from deposits closely related genetically but occurring in different geological settings, and also from deposits of different types (Table 1).

The first six analyses in Table 1 are of galenas from lead and lead-zinc deposits; analyses 3, 4 and 5 are of samples from a new deposit areally related to extrusive rocks (Alaityr) and from a recently discovered mineralization in limestones (metallometric point). Six measurements (7-12) were made on galena and cosalite from deposits of rare metals for which there were no data on the isotopic composition of lead. Two analyses (16 and 17) are of lead from manganese deposits which also had not been analyzed. The first eight determinations listed in Table 1 were made on lead from deposits lying close to one another (within a radius of 100 km) within a single region (Northern Balkhash region) and possibly formed during the same episode of mineralization. Analysis 13 was made on galena from D_3--C_1 limestones located about 5 km to the southwest of the Kara-Oba deposit. The Bes-Tyube deposit (analysis 14), 35 km southwest of the Kuzhal deposit, is a thick barite lens with disseminated galena. The data on this deposit have already been published [2, 3]. The newly discovered Melkosopochnoe occurrence (Sambai deposit), 30 km to the south southeast of the Kuzhal

Table 1

Isotopic Composition of Lead from Various Ore Deposits of Control Kazakhstan

No.	Locality	Brief characteristic of the deposit	$\frac{Pb^{206}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{204}}$	$\frac{Pb^{208}}{Pb^{204}}$	$\frac{Pb^{207}}{Pb^{206}}$
1	Aksoran, East[1]	Disseminated galena in marble	18.29	15.79	38.60	0.863
2	Aksoran, West[1]	Disseminated galena in gray limestone	18.36	15.82	38.67	0.862
3	Alaigyr, Upper[1]	Disseminated galena and pyrite in quartz porphyries	17.99	15.47	37.86	0.860
4	Alaigyr, Lower[1]	Very fine dissemination of galena in the feldspars of the extrusives	18.01	15.47	37.83	0.859
5	Metallometric Point	Thin veinlets and nests of galena in limestone	18.02	15.48	38.03	0.859
6	Akdzhal	Lead-zinc mineralization in D_3 limestones	18.07	15.62	38.20	0.864
7	Akchatau	Galena associated with low quartz from high temperature veins	17.99	15.44	37.79	0.858
8	Zhanet	Galena from later veinlets and segregations	17.94	15.43	37.88	0.860
9	Shalgiya	Galena from later veinlets and segregations	18.04	15.67	38.47	0.869
0	Kara-Oba	Galena ⎫ Later minerals of high temperature veins	18.03	15.37	37.37	0.852
1	Kara-Oba[2]	Cosalite ⎭	17.94	15.39	37.47	0.858
2	Kara-Oba[2]	Galena. Small inclusion in feldspar from a high temperature vein	18.09	15.47	37.35	0.855
3	Kara-Oba region[2] (5 km southwest of deposit)	Galena from a quartz-calcite veinlet in D_3-C_1 limestones	18.04	15.40	37.52	0.854
4	Bes-Tyube	Galena. Inclusions in barite	18.09	15.66	38.05	0.866

Table 1 (Cont'd.)

Isotopic Composition of Lead from Various Ore Deposits of Control Kazakhstan

No.	Locality	Brief characteristic of the deposit	$\dfrac{Pb^{206}}{Pb^{204}}$	$\dfrac{Pb^{207}}{Pb^{204}}$	$\dfrac{Pb^{208}}{Pb^{204}}$	$\dfrac{Pb^{207}}{Pb^{206}}$
15	Sambai	Galena from the fracture zone in chloritized sandstones (S)	18.05	15.65	37.94	0.867
16	Dzhezdy	Lead separated from manganese ore	17.93	15.64	37.87	0.872
17	Zhana-Bek	Lead from oxidized manganese ore	17.99	15.69	38.14	0.872

[1] Specimens donated by Yu. A. Borshchevskii
[2] Specimens donated by I. G. Ganeev

deposit, consists of sphalerite, chalcopyrite and galena disseminated through a fractured zone in chloritized Silurian sandstones (analysis 15).

The new data for the Aksoran deposit agree very well with the previously published analysis [3]. But our analysis of a sample from the Akzhal deposit differs from the analysis reported earlier [1], which showed the lead to be anomalous in composition with a high Pb^{206} and Pb^{207} content and a low Pb^{207}/Pb^{206} ratio. There is a similar disagreement for the Gul'shad deposit [2, 4]. The reason for these discrepancies is not clear at present. These deposits require further investigation.

The determinations of the isotopic composition of lead were made on the mass spectrometer MC-3. Analyses of samples 1-12 and 16-17 were made on lead iodide in mass spectra with peaks at 202-208 and 331-335. Samples 13, 14 and 15 were made by direct introduction of galena into the ion source by the method described earlier [5, 6]. The error in the determination of all lead isotopes was somewhat less than $\pm 1\%$.

Of especial interest are the analyses of samples from the deposits of manganese and rare metals. The outcrops of manganese mineralization at Zhan-Bek consist of oxidized manganese ores and lie in the same beds of the D_3 limestones as the disseminated galena, the composition of whose lead has already been reported [2]. The sample of galena was taken from the immediate vicinity of the manganese occurrence. The manganese ores of Zhan-Bek are interesting because they are enriched in lead (up to several percent), thallium, etc. The form in which lead occurs in the ores is not known; galena is absent. For the analysis, lead was extracted chemically. The composition of lead from the manganese locality is identical with that from galena. At the Dzhezda manganese deposit, some of the ore bodies are also enriched in lead and thallium, which are concentrated mainly in psilomelane. Galena is absent from the ores. The composition of lead (analysis 16) extracted from the ore chemically is identical with the composition of lead from the Zhan-Bek manganese ore, although these two

ocalities are at a considerable distance from each other. (The Zhan-Bek
prospect lies 350–300 km to the north northeast of the Dzhezda deposit.)
The origin of the Dzhezda deposit is controversial. In the latest work de-
voted to this subject, A.A. Maksimov [7] considers it as an infiltration
deposit. The problem of the origin of lead and the associated thallium re-
mains unsolved. But the close similarity in isotopic composition of lead
from the manganese ores and from the hydrothermal deposits discussed in
the present and previously published papers [2, 3] suggests that the lead in
the manganese ores is also hydrothermal. It is possible that the lead in
the manganese ores is the result of redeposition of the primary hydrother-
mal lead. This hypothesis, however, requires a special study.

As a rule, in all high temperature deposits of rare metals, the later
lower temperature processes are manifested to a greater or less degree.

Various sulfides, particularly galena and infrequently cosalite, are the
products of these processes. The deposits of rare metals (Akchatau,
Chanet and Kara-Oba) have much in common with many other deposits of
this type and according to all available data are related to the intrusions of
leucocratic granites, alaskites.

The problem of the Shalgiya deposit is more complex. This is a lower
temperature molybdenum mineralization in the form of a stockworks of
quartz veins and veinlets in silicified and sericitized granite. There are
no greisen; molybdenite occurs in very fine particles and gives quartz a
peculiar bluish tinge. The question of genetic relation between the deposit
and one of the granitic intrusions (Munglu or Kuu) has been only tentatively
answered. But in this deposit also the appearance of lead and zinc sulfides
is clearly separated from the main stage of mineralization by a period of
movement and fracturing. The drill hole data establish spatial independ-
ence of some of the late sulfide veinlets. It was believed that the low tem-
perature phases in deposits of rare metals were a part of the normal devel-
opment, the end of deposition of rare metals. The possibility of superimpo-
sition of a polymetallic phase, now often accepted as a part of the process
of skarn formation, was not considered. Yet, as we showed for the pegma-
tites of Karelia, the low temperature mineralization may be superimposed
after a considerable interval of time [8]. It was interesting, therefore, to
determine the isotopic composition of lead from this latest hydrothermal
phase in the deposits of rare metals and to compare it with the composition
of lead from the common lead and other deposits and also with the composi-
tion of lead in granites. The results of analysis of specimens from the de-
posits of rare metals are given in Table 1 (analyses 7-12). The analyzed
samples from the Kara-Oba deposit include galena from an intermediate
temperature wolframite vein, small inclusions of galena from feldspar of
the high temperature wolframite-quartz-feldspar vein and cosalite from the
same vein. An analysis was also made of galena from the skarn in the
limestones at a new lead prospect near the Kara-Oba deposit (5 km to the
southwest) (analysis 13). The compositions of these leads are identical.
Moreover, they are exactly like the composition of leads from numerous
deposits and occurrences of other genetic types.

The lowest age limit (or the maximum possible age) is known exactly
for most of the deposits of Central Kazakhstan on the basis of the known age
of the enclosing rocks. But this limit does not give the actual age of the
deposit itself. In some cases, for example for the Kurgasyn deposit, this
is quite obvious from the isotopic composition of lead, which indicates that
the ore is much younger than the enclosing Precambrian rocks [2]. Esti-
mates of the age of deposits on the basis of the age of the country rock may

lead to incorrect conclusions. For many of the lead and other deposits of Central Kazakhstan, the composition of whose leads have been studied, the lower age limit is D_3-C_1. The age of the Akchatau and Zhanet deposits has been rather accurately determined as 300.10^6 years [9, 10]. According to the existing, although not very accurate, data, this corresponds to Middle Devonian. This age may be taken either as the actual age of the polymetallic phase of the rare metals mineralization or as only the possible lower limit of it. In the first case, a genetic unity (of one form or another) of the entire mineralization process is assumed; in the second, the polymetallic phase is considered as superimposed upon the primary mineralization after a long interval of time. The Akdzhal deposit, 40 km distant from the Akchatau deposit, has lead of the same isotopic composition according to our data (see above) as the Akchatau and Dzhanet deposits although it lies in the D_3 limestones. Genetic unity of the leads from these deposits is very probable; their composition is very similar to that of the leads from two other deposits--Alaigyr and Metallometric Point, lying 150 km to the northeast. On the other hand, the lower age limit for the distant Dzhezkazgan deposit also characterized by a practically identical composition of lead, is determined as C_2 (C_2--P_1?). This is also the highest known age limit. The lack of even a single deposit for which the upper age limit is definitely known (or simply the age of the deposit) makes it impossible to speak with certainty of the age of mineralization as a whole, which may be younger than C_1. It is impossible to judge by the isotopic composition of lead in this case. If the deposits within a region having identical isotopic composition of lead are practically contemporaneous, which is very probable, then the lower age limit of the Dzhezkazgan deposit, C_2, supports the probability of superimposition of the polymetallic phase in the deposits of rare metals. A convincing confirmation would be the difference in composition of the lead from granites to which the deposits are related and of the lead from the latest phases of mineralization. But identity in the composition of these leads will not be a full proof of genetic connection, but will merely indicate the possibility of such a relationship (see also the conclusions of A. P. Vinogradov et al [3]). To prove the superimposed character of the low temperature phases of the rare metals mineralization in light of the available data is impossible, and we must limit ourselves merely to posing the question.

According to three consistent determinations, the Aksoran deposit, located at about the same distance from Akchatau as the Akdzhal deposit, differs from the latter slightly in the composition of its lead. But this difference lies within the limits of experimental error. Great caution is necessary, therefore, in drawing conclusions concerning the presence in a deposit of lead derived from different sources. A clearer difference is found in a group of deposits located at a distance of several tens of kilometers from the Kuzhal deposit. Comparison of the composition of their leads is given in Table 2. The first two analyses in the table differ from all others in having a relatively high content of Pb^{206}, Pb^{207} and Pb^{208} while preserving the Pb^{207}/Pb^{206} ratio; i.e., there is no apparent anomaly of composition. The first four deposits are undoubtedly hydrothermal. The origin of the Bes-Tyube deposit, or, more exactly, of its lead mineralization, is not clear. However, the similarity of composition between its lead and the lead from the nearby hydrothermal deposits suggests common origin of the metal. It is possible that these two groups of deposits differ in age, as well, but the difference cannot be estimated from the isotopic composition of their leads. Nor can it be determined which mineralization is the

Table 2

Isotopic Composition of Lead from the Ore Deposits of the Kuzhal Region

Locality	$\dfrac{Pb^{206}}{Pb^{204}}$	$\dfrac{Pb^{207}}{Pb^{204}}$	$\dfrac{Pb^{208}}{Pb^{204}}$	$\dfrac{Pb^{207}}{Pb^{206}}$
zhal	18.51	16.10	39.28	0.869
ad ore occurrence 9 km southwest of the Kuzhal deposit	18.54	16.06	39.30	0.867
ld ore occurrence 26 km southwest of the Kuzhal deposit	17.93	15.48	38.19	0.864
nbai. Peschanye Sopki area, 30 km south southeast of the Kuzhal deposit	18.05	15.65	37.94	0.867
s-Tyube, 35 km southwest of the Kuzhal deposit	18.09	15.66	38.05	0.866

lier. Inasmuch as within the boundaries of a region, and especially
lin individual deposits, leads with relatively high Pb^{206}, Pb^{207} and
^{08} content are later than the leads with lower content of these isotopes,
s possible that the mineralization of the first two deposits is later than
t of the others. In any case, the areal proximity of the deposits makes
robable that one of them, or some other still undiscovered deposit, will
d two different leads, i.e. two generations of galena.
The authors express their gratitude to A. A. Maksimov for his guidance
help and to I. G. Ganeev and Yu. A. Borshchevskii for aid in the selec-
l of samples.

Summary

1. The isotopic composition of 17 samples of lead from 15 different
osits of Central Kazakhstan has been studied.
2. A number of leads from manganese, rare metals and hydrothermal
osits have identical isotopic composition.
3. It is possible that the polymetallic phase of mineralization in rare
tals deposits is superimposed and may be genetically related to the
mation of lead, lead-zinc and other deposits.
4. Genetically related deposits located not far from one another have
ds of different isotopic composition. It is probable that in these deposits
l in the deposits within a given region the presence of two generations of
ena will be established.

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CHEMICAL AND GEOCHEMICAL
CHARACTERISTICS OF THE
CAMBRIAN EXTRUSIVES OF TUVA

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Problems of the chemistry and geochemistry of the igneous rocks of the
i-Sayan region have so far received almost no attention. This is espe-
ly true of the volcanic rocks, which in general have been very little
ied. Suffice it to say that in the rather extensive literature devoted to
igenous rocks of the Altai-Sayan region only two papers (Monich, 1937,
i) can be cited which, to a certain extent, touch upon the chemistry of
ent intrusive and extrusive rocks, predominantly in the Kuznetskii
au region.

Having been occupied during the past few years with an investigation of
igneous geology of Tuva, and of its Cambrian volcanics in particular,
author had an opportunity to gather pertinent material and partly fill the
in the knowledge of the chemistry and geochemistry of these Cambrian
usives.

The early stages of development of the Caledonian geosyncline in Tuva
in the Altai-Sayan region as a whole were characterized by intensive
anic activity resulting in the accumulation of thick sedimentary-
anic sequences which now form, together with associated intrusives
basement of this geotectonically complex region.

general geological description of the Cambrian extrusives will be
d in Zaitsev and Pokrovskaya (1950), Kudryavtsev (1950), Kuznetsov
3), Leontev (1956), and Maslov, (1947); without reviewing these papers
all pass to a discussion of the chemical characteristics of these
usives.

The chemical description of the Cambrian extrusives is based on 26
plete silicate analyses of typical representatives of these rocks from
rent parts of Tuva. With these analyses, which are given in Table 1,
author constructed a vector diagram using Zavaritskii's method (Fig. 1).
n examination of the diagram shows that the analyzed Cambrian extru-
s of Tuva are very similar in their composition to the typical lavas of
calc-alkalic association and are, therefore, products of calc-alkalic
ma. A detailed analysis of the diagram shows certain deviations of the

Table 1

Chemical Composition of the Extrusive Rocks of Tuva

Rock	Percent by weight													
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	Misc.	sum
Amygdaloidal basalt	46,70	1,20	18,28	2,72	9,83	0,21	8,50	2,76	2,81	2,23	0,21	—	4,65	100,19
Basaltic andesite	47,74	2,06	16,30	4,15	9,05	0,22	6,72	10,82	3,04	0,30	—	0,16	1,94	99,68
Amygdaloidal basaltic andesite	45,28	1,50	11,61	3,89	9,00	0,16	10,22	14,30	1,36	0,77	—	—	2,54	100,63
Basaltic andesite	48,10	1,15	20,36	2,65	8,59	0,19	3,92	19,07	3,03	0,73	—	—	1,34	100,22
Amygdaloidal basalt	44,80	2,50	13,19	2,14	9,47	0,18	10,79	8,79	2,49	1,09	—	0,04	3,50	99,26
Uralitized basalt	47,90	0,90	17,02	0,86	9,29	0,16	11,94	7,39	2,36	0,22	—	0,01	2,66	100,80
Basaltic andesite	49,58	0,80	16,77	1,50	9,43	0,09	9,49	6,95	2,46	0,51	—	0,20	2,66	100,44
Basalt	47,07	2,24	17,53	5,07	6,58	0,16	5,93	8,55	1,43	0,58	—	—	2,99	100,61
Augite andesite	50,72	0,62	14,10	1,32	6,79	0,11	11,77	8,63	2,76	0,80	0,18	—	3,21	99,73
Augite andesite	51,20	1,10	18,52	6,18	3,25	0,18	4,02	8,22	1,76	1,31	—	0,44	2,20	99,38
Labradorite andesite	53,70	1,59	18,13	4,47	4,02	0,14	3,96	7,76	3,33	2,46	—	0,12	1,02	99,80
Amygdaloidal plagioclase andesite	50,52	2,72	17,80	3,57	7,01	0,09	3,13	8,59	1,47	2,10	0,22	—	2,36	99,74
Amygdaloidal plagioclase andesite	51,62	1,18	16,73	7,97	2,74	0,31	4,74	7,41	2,50	1,10	—	0,64	2,14	99,43
Plagioclase andesite	52,26	0,85	19,05	8,65	3,02	0,11	2,42	8,30	2,12	1,39	0,21	—	0,60	99,20
Plagioclase andesite	53,06	1,28	16,41	6,27	3,45	0,16	4,30	7,40	3,13	2,11	—	—	1,82	99,42
Plagioclase andesite	53,10	0,90	19,17	2,70	9,07	0,42	5,91	0,10	2,04	1,30	—	—	4,81	99,25
Hornblende-andesite	56,71	1,07	17,05	3,62	4,66	0,14	3,63	6,00	3,09	1,94	0,25	0,20	1,45	99,50
Amygdaloidal plagioclase andesite	57,96	0,59	17,50	2,92	6,46	0,45	0,84	4,58	2,61	3,73	0,32	0,20	2,10	99,76
Plagioclase andesite	51,04	1,12	18,77	4,89	2,60	0,10	6,23	7,55	4,09	0,19	—	0,34	3,04	99,96
Plagioclase andesite	65,50	1,12	14,79	4,81	0,40	0,09	1,00	2,89	4,87	1,55	—	0,17	2,43	99,62
Rhyolite	72,48	0,24	13,66	0,86	3,13	0,06	0,64	1,08	3,01	5,09	0,07	0,40	—	100,40
Rhyolite	70,94	0,57	14,49	2,66	0,16	0,04	0,04	0,74	5,41	2,95	—	0,26	1,16	99,44
Felsite	72,30	0,20	17,68	1,50	3,30	0,04	0,26	1,07	3,19	5,61	0,04	0,10	—	100,21
Albitophyre	75,20	0,33	11,88	1,84	1,49	0,16	0,22	0,84	5,96	0,07	—	0,16	1,16	99,24
Keratophyre	61,04	0,06	18,70	0,87	6,93	0,12	0,34	0,49	4,62	6,67	—	—	0,80	100,57
Keratophyre	60,78	0,50	17,15	0,71	4,68	—	2,87	3,02	6,31	0,72	—	—	3,46	100,20

Note: Analyses performed in the Chemical and Metallurgical Institute of the West Siberian Affiliate of the Academy of Sciences USSR, the Geological Institute of the Academy of Sciences and in the Central Chemical Laboratory of the West Siberian Geological Bureau by A. Popova, K. Sokova, M.A. Keperabtein and Z.I. Astopovich.

Note: Comma represents decimal point.
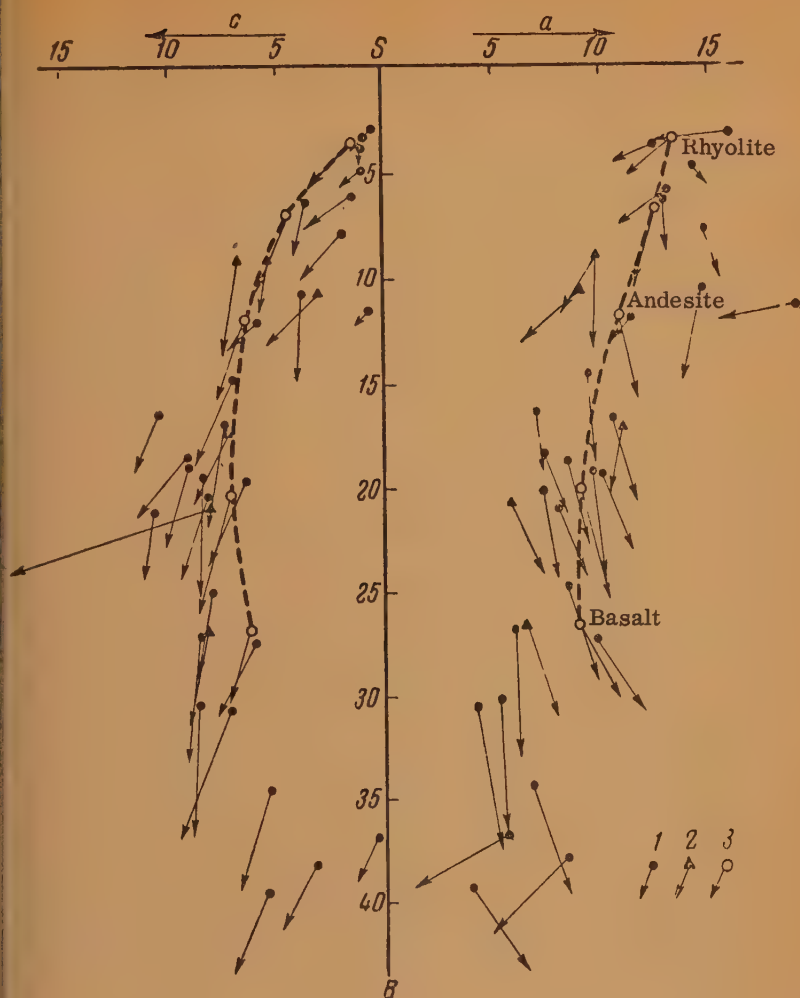
Fig. 1. Vector diagram. Composition of the Cambrian
extrusives of Tuva:

1 -- Cambrian extrusives; 2 -- Devonian extrusives;
3 -- variation curve of average extrusive rocks
after Daly (1933)

oup of vectors representing the composition of the Cambrian extrusives
Tuva from the variation curve of typical calc-alkalic lavas. In the lower
rt of the diagram in both projections, most of the composition vectors of
e Tuvan rocks lie to the left of the variation curve, while in the upper part

of the diagram they lie to the right of it. This position of the origins of
vectors indicates that the mafic extrusives of the series are somewhat
poorer in alkalies and richer in calcium (as anorthite), as compared with
the typical rocks of the calc-alkalic volcanic associations. With increase
in silica content, the picture is reversed; i.e., in the felsic Cambrian ex-
trusives of Tuva, the amount of alkalies (as aluminosilicates) is greater,
while the content of calcium (as feldspars) is less as compared with typical
felsic calc-alkalic lavas. Further, if the change in direction of the vectors
from mafic to felsic rocks is traced on the right side of the diagram, it will
be noticed that in many cases there is no gradual rotation of the vectors to
the left. This is particularly characteristic for typical calc-alkalic lavas,
especially in the upper part of the ASB projection. Therefore, increase in
alumina with increase in silica content is less pronounced in the Cambrian
Tuvan lavas than in typical calc-alkalic lavas. Finally, still another pecu-
liarity of the Cambrian extrusives of Tuva may be noted, expressed by the
steepness of vectors on the left side of the diagram, which indicates a
strong predominance of sodium over potassium, especially in the mafic and
intermediate rocks.

That the Cambrian Tuvan lavas belong to a single reaction series, devel-
oped from a single magmatic source, is proven by both their areal distribu-
tion (alternation of felsic, intermediate and mafic rocks) and the data given
in Table 2.

An examination of the table reveals a regular change in the chemical
composition of the rocks during the course of their differentiation from a
primary basaltic magma. As the rocks become more siliceous, the content
of lime decreases noticeably, with increase in alkalies; the importance of
potassium grows steadily. An exception to this is the sharp increase in
sodium in the albitophyres and keratophyres due to postmagmatic albitiza-
tion. An important index in the differentiation of basaltic magma is the
ratio between iron and magnesium oxides. The table shows clearly the in-
crease in iron and decrease in magnesium in the basalt-rhyolite series.

Thus, the regular change in chemical composition of the rocks from
mafic to felsic and their areal distribution serve as sufficient evidence for
(1) the existence of a single magmatic source in the Lower Cambrian and
(2) the basaltic composition of the primary magma which gave rise by the
process of differentiation to all varieties of Cambrian extrusives of Tuva.

It should be noted that the average composition of Cambrian basalts and
basaltic andesites of Tuva is somewhat different from averages given by
Daly (Table 3).

According to the table, this difference is mainly the lower silica content
of the Tuvan basalts (9.7 as against 3.6), a somewhat higher alumina and
especially magnesia content, and a somewhat lower alkali content. There
is practically no difference in the total iron content. It follows from this
that the Cambrian basaltic rocks of Tuva, usually found in the lower part
of the Cambrian sedimentary-volcanic sections, are highly mafic and were
evidently crystallized from a magma which was only slightly differentiated.

The chemical characteristics of the Tuvan lavas given so far are based
on the content of major elements and their ratios. For a fuller analysis of
the composition of these rocks and discovery of additional characteristics,
it is interesting to examine the distribution of trace elements in them. For
this purpose, 156 semiquantitative spectrographical analyses were made
for the following elements: Mn, Ni, Co, Ti, V, Cr, Mo, W, Zr, Nb, Ta,
Cu, Pb, Ag, Sb, Bi, As, Zn, Cd, Sn, Ge, Ga, In, Be, Sc, P, Li, Sr, Ba,
Au, Pt, Tl and Te. The elemental concentrations were estimated by the

Average Chemical Composition of Cambrian Extrusives

	CaO	Na$_2$O+ K$_2$O	Na$_2$O:K$_2$O	FeO:MgO	SiO$_2$
Basalts and basaltic andesites (8 analyses)	8,74	3,42	4,66	0,76	47,15
Augite and labradorite andesites (3 analyses)	8,05	3,89	2,66	0,70	51,87
Plagioclase andesites (9 analyses)	5,88	4,60	2,55	1,24	54,64
Albitophyres, keratophyres (3 analyses) Rhyolites, felsites (3 analyses)	1,44 0,96	8,12 8,42	3,37 1,27	2,66 7,29	65,67 71,91

Note: Oxide ratios are given in molecular proportions, the rest of the data, in percent by weight.

Table 3

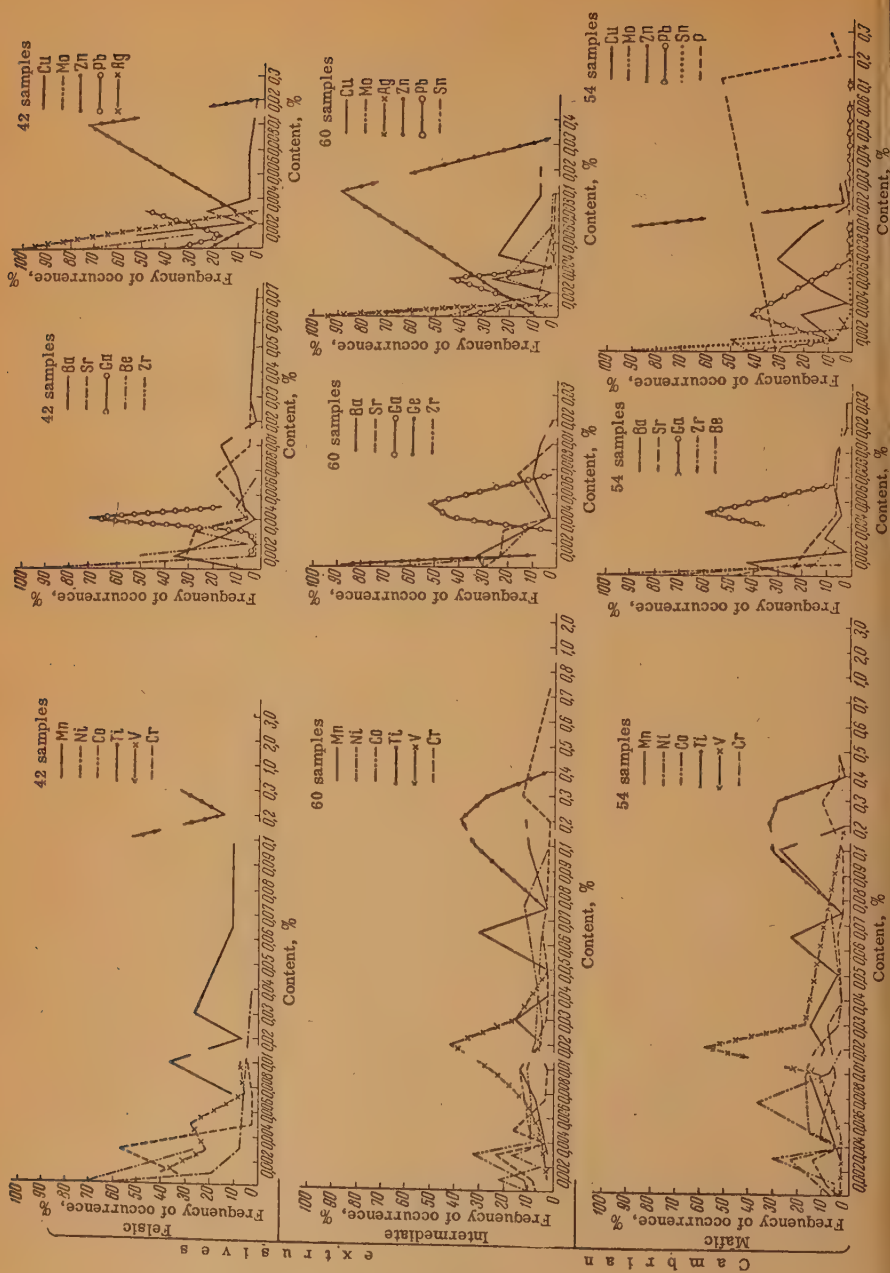| Oxides / Rocks	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	FeO	MnO	MgO	CaO	Na$_2$O	K$_2$O
Average basalt (after Daly 1933)	50,48	1,45	15,34	3,84	7,78	0,20	5,79	8,94	3,07	0,97
Average composition of Tuva basalt (8 analyses)	47,15	1,54	16,38	2,87	8,91	0,17	8,44	3,74	2,62	0,80

Note: Comma represents decimal point.

Fig. 2.
Frequency
of occur-
rence and
content of
trace ele-
ments in the
Cambrian
extrusives
of Tuva
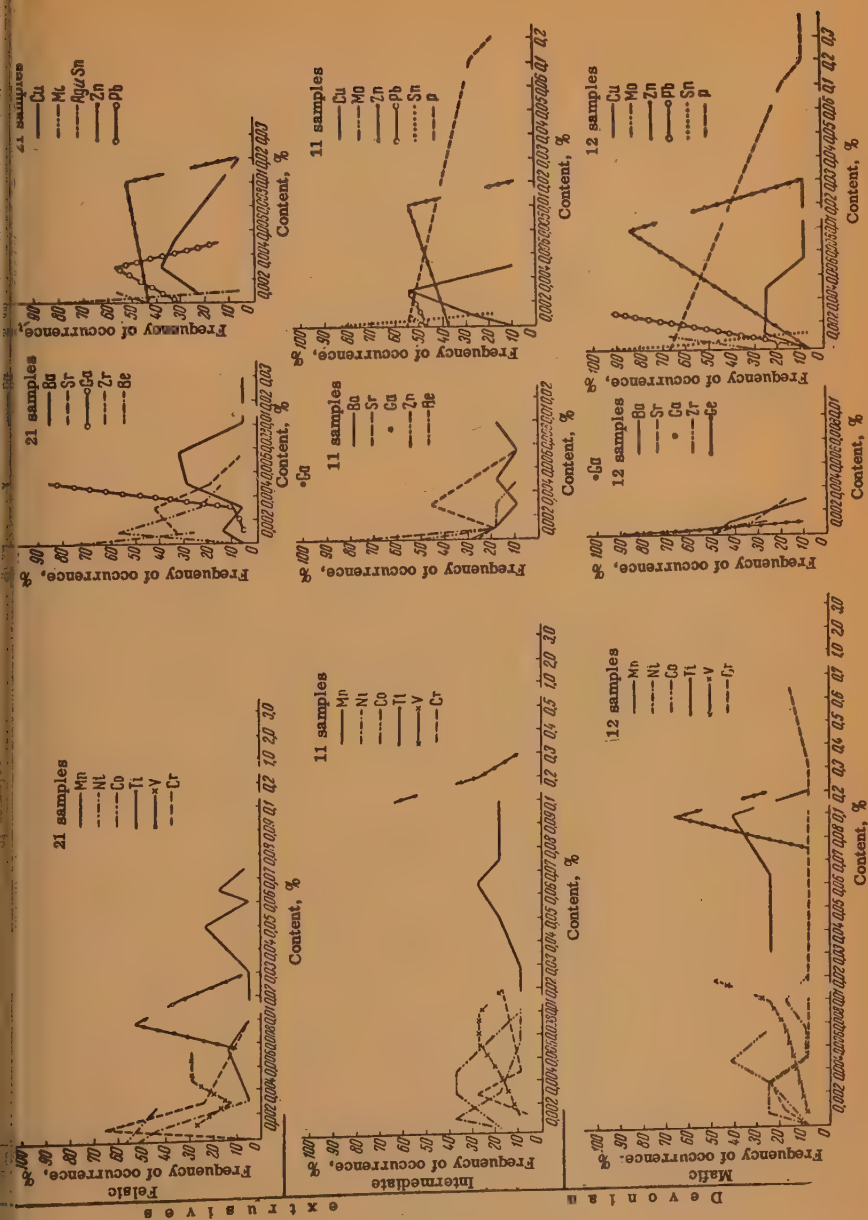
Fig. 2.
Frequency of occurrence and content of trace elements in the Devonian extrusives of Tuva

Table 4

Average Content of Elements in the Cambrian Extrusives of Tuva

	Elements / Extrusives	Mn	N	Co	Ti	V	Cr	Cu
Camb.	Felsic	299,4	13,5	7,9	1809,5	36,5	30,0	26,4
	Intermediate	396,6	70,9	51,1	1941,6	170,6	518,6	235,1
	Mafic	573,8	90,2	77,2	2104,6	218,2	977,4	66,2
Devon.	Felsic	533,6	5,7	12,8	928,1	42,9	18,6	40,0
	Intermediate	795,5	43,2	20,0	1454,5	94,1	53,6	23,6
	Mafic	820,8	53,7	47,1	1312,5	138,3	546,6	53,7

Note: Comma represents decimal point.

intensity of diagnostic spectral lines (Prokof'ev 1937). A table giving element wavelengths and intensities as a function of concentration was prepared from analyses of standard mixtures with a silicate base and from published data (Kalinin et al., 1957). The 20 mg samples were evaporated from cavities in carbon electrodes in an activized a.c. arc at 8-9 amperes and 220 volts. The distance between the electrodes was 4 mm. The spectra were photographed on the Hilger spectrograph of medium dispersion with 0.02 mm slit.

Of the 33 elements listed above, 14 (W, Nb, Ta, Sb, Bi, Cd, In, Sc, Li, Au, Pt, Tl, Te and As) were not detected in any of the samples. A few samples contained Sn, Ag, Ge and B. The rest of the elements were present in most of the samples, and Mn, Ti, Cu and Ga, in all samples without exception. The content of individual trace elements in Cambrian extrusives of Tuva is shown in Figs. 2 and 3. The average content of the elements in grams per ton in mafic, intermediate and felsic lavas is given in Table 4.

An examination of the table shows that there is a definite pattern in the distribution of the trace elements depending on the degree of maficity of the lavas. The content of the iron group elements increases uniformly from felsic through intermediate to mafic rocks, and the concentration of such elements as Ni, Co, V, and Cr increases from 6 to 32 times. Phosphorus behaves in a similar manner. Its content in the mafic extrusives is 37 times as great as in the felsic. The same can be said of Pb, Mo and Ga, although the difference between the content of these elements in felsic and mafic lavas is not as great. The increase in the gallium content, for example, is only 18%. A reverse relation between the content of elements and silica content of the lavas is shown by zirconium, barium and strontium. The concentration of these elements in the felsic extrusives is from 2 to 7 times as great as in the mafic. It must be noted that the sharpest change in the content of trace elements is observed between felsic and intermediate

Table 4 (Cont'd.)

Zn	Pb	Mo	Zr	Ga	Ba	Sr	P	Be	Ge	Sn	Ag
105,2	15,9	2,9	22,9	39,3	72,5	50,5	23,8	0,95	—	—	0,7
100,0	23,4	9,2	6,3	46,2	32,0	39 8	583,3	—	0,8	3,4	0,2
114,8	44,1	7,0	3,1	47,9	30,2	21,1	925,9	0,4	—	0,5	—
61,9	24,3	5,7	22,0	46,2	70,7	29,3	—	0,5	—	0,5	0,5
72,7	16,3	5,4	11,8	50,0	38,6	22,2	636,3	1,8	—	1,8	—
108,3	2,5	6,6	2,5	50,0	6,6	8,3	777,7	—	0,1	2,5	—

Note: Analytical work performed in the spectrographic laboratory of the Institute of Geology and Geophysics of the West Siberian Affiliate, Academy of Sciences USSR, by analysts N. V. Arnautov and L. D. Shipilov.

Note: Comma represents decimal point.

lavas. The difference in concentration of these elements in intermediate nd mafic rocks is relatively small. The concentration of copper in felsic lavas is on an average only 2. 5 times less than in mafic. Copper is strongly enriched in intermediate lavas. Indeed copper mineralization is genetically and specifically related to andesites in the Tuva rocks. As for zinc, its content is about the same in all three types of extrusives. In the felsic lavas zinc is 5% higher than in intermediate rocks; in mafic lavas :5% higher. Traces of beryllium were found in individual samples of felsic nd basic rocks; its content in felsic rocks does not exceed . 003% and in mafics 0. 001%. Tin and germanium were not found in felsic lavas; germanium was absent also from basic rocks. The tin content in some samples is as high as 0. 02%, but in most samples it is 0. 001%. Up to 0. 003% silver was found in a few felsic and intermediate rocks.

The presence of the same assemblage of trace elements in Cambrian Tuvan lavas of different composition is still another proof of their common source. The regular variation in the content of related elements from mafic to felsic rocks indicates differentiation of the parent magma.

Interesting data were obtained by comparing the content of elements in the Tuvan lavas with the average content of the same elements in the felsic, intermediate and mafic rocks of the earth's crust (Vinogradov, 1956). These data are given in Table 5.

The agreement between the two sets of data is satisfactory, especially if it is remembered that, in calculating the average elemental composition for the different rock groups in the earth's crust, analyses of both intrusive and extrusive rocks were used. It is well known that the two types of rocks differ somewhat in composition. This agreement serves to some extent as a check on the accuracy of the spectrographic analyses which were used in the present work.

It remains to compare the Cambrian extrusives of Tuva with the Lower Devonian volcanic rocks, which are rather widespread in the Middle

Table 5

Elements	Felsic rocks		Intermediate rocks		Mafic rocks	
	extrusives of Tuva	average for the crust	extrusives of Tuva	average for the crust	extrusives of Tuva	average for the crust
	Content, % by weight					
Mn	$3 \cdot 10^{-2}$	$6 \cdot 10^{-2}$	$4 \cdot 10^{-2}$	$1,2 \cdot 10^{-1}$	$5,7 \cdot 10^{-2}$	$2,2 \cdot 10^{-1}$
Ni	$1,3 \cdot 10^{-3}$	$8 \cdot 10^{-4}$	$7,1 \cdot 10^{-3}$	$5,5 \cdot 10^{-3}$	$9 \cdot 10^{-3}$	$1,6 \cdot 10^{-2}$
CO	$7,9 \cdot 10^{-4}$	$5 \cdot 10^{-4}$	$5,1 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$7,7 \cdot 10^{-3}$	$4,5 \cdot 10^{-3}$
Ti	$1,8 \cdot 10^{-1}$	$2,3 \cdot 10^{-1}$	$1,9 \cdot 10^{-1}$	$8 \cdot 10^{-1}$	$2,1 \cdot 10^{-1}$	$9 \cdot 10^{-1}$
V	$3,6 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	$7,1 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	$2,2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$
Cr	$3 \cdot 10^{-3}$	$2,5 \cdot 10^{-3}$	$5,2 \cdot 10^{-2}$	$5,6 \cdot 10^{-3}$	$9,8 \cdot 10^{-2}$	$3 \cdot 10^{-2}$
Cu	$2,6 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$2,4 \cdot 10^{-2}$	$3,5 \cdot 10^{-3}$	$6,6 \cdot 10^{-3}$	$1,4 \cdot 10^{-2}$
Zn	$1 \cdot 10^{-2}$	$6 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$7,2 \cdot 10^{-3}$	$1,1 \cdot 10^{-2}$	$1,3 \cdot 10^{-2}$
Pb	$1,6 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$2,3 \cdot 10^{-3}$	$1,5 \cdot 10^{-3}$	$4,4 \cdot 10^{-3}$	$8 \cdot 10^{-4}$
Mo	$2,9 \cdot 10^{-4}$	$1,9 \cdot 10^{-4}$	$9,2 \cdot 10^{-4}$	$9 \cdot 10^{-5}$	$7 \cdot 10^{-4}$	$1,4 \cdot 10^{-4}$
Zr	$2,3 \cdot 10^{-3}$	$2 \cdot 10^{-2}$	$6,3 \cdot 10^{-4}$	$2,6 \cdot 10^{-2}$	$3,1 \cdot 10^{-4}$	$1,10 \cdot 10^{-2}$
Ga	$3,9 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$4,6 \cdot 10^{-3}$	$2,0 \cdot 10^{-3}$	$4,8 \cdot 10^{-3}$	$1,8 \cdot 10^{-3}$
Ba	$7,3 \cdot 10^{-3}$	$8,3 \cdot 10^{-2}$	$3,2 \cdot 10^{-3}$	$6,5 \cdot 10^{-2}$	$3 \cdot 10^{-3}$	$2,7 \cdot 10^{-3}$
Sr	$5,1 \cdot 10^{-3}$	$3 \cdot 10^{-2}$	$4 \cdot 10^{-3}$	$8 \cdot 10^{-2}$	$2,1 \cdot 10^{-3}$	$4,4 \cdot 10^{-2}$
P	$2,4 \cdot 10^{-3}$	$7 \cdot 10^{-2}$	$5,8 \cdot 10^{-2}$	$1,6 \cdot 10^{-1}$	$9,3 \cdot 10^{-2}$	$1,4 \cdot 10^{-1}$

Note: Comma represents decimal point.

Table 6

Chemical Composition of the Devonian Extrusives of Tuva

Rock	Weight percent												
	SiO₂	TiO₂	Al₂O₃	Fe₂O₃	FeO	MnO	MgO	CaO	Na₂O	K₂O	H₂O	misc.	sum
Augite andesite	47,14	2,27	16,35	5,72	5,28	0,22	6,88	9,48	2,33	0,76	0,62	2,38	99,43
Amygdaloidal basalt	50,76	2,90	13,43	2,05	8,43	0,25	3,77	7,23	0,58	2,81	0,53	7,34	100,08
Labradorite andesite	48,50	2,24	17,68	6,69	3,59	0,17	3,04	5,43	3,12	2,27	0,48	6,36	99,32
Hornblende andesite	63,27	0,40	17,05	1,28	3,71	0,08	2,48	5,29	3,79	1,02	0,04	1,96	100,37
Plagioclase andesite	65,11	0,40	16,04	3,80	2,00	—	1,33	4,08	3,92	0,91	0,22	2,54	100,35
Rhyolite	66,61	0,52	13,32	3,82	2,00	0,12	1,46	2,29	2,10	3,08	0,16	4,08	99,56

Note: Comma represents decimal point.

Paleozoic downwarp superimposed on the Salair basement (Table 6). The comparison between the Cambrian and Devonian lavas is not only of theoretical interest but practical also, because in some regions of Tuva as a result of special conditions of formation, it is practically impossible to distinguish Cambrian from Devonian volcanics.

In addition to data on composition of the Cambrian extrusives, the variation diagram (Fig. 1) shows vectors corresponding to the composition of typical representatives of Devonian lavas. In comparing the positions of the vectors of Cambrian and Devonian lavas of Tuva, several differences become apparent: 1) The mafic Devonian lavas are poorer in the elements entering into the femic constituents than their Cambrian counterparts. The maximum value of parameter B, which reflects this feature of rock chemistry, is 26.8% in the Devonian lavas and 39.5% in the Cambrian. 2) The femic constituents in mafic Devonian extrusives are richer in iron, contain less magnesium and have a relatively higher content of free calcium than the analogous mafic Cambrian lavas. These differences are reflected on the lower right of the diagram by the relative shortness and lesser steepness of the vectors representing Devonian rocks. 3) The Devonian extrusives are poorer in alkalies and the felsic Devonian lavas are richer in alumina than their Cambrian analogues. These characteristics of the Devonian lavas are reflected in the diagram by the shifting of the vectors on the ASB projection to the left and in the sharp rotation of the vectors of the felsic Devonian rocks in the same direction.

An examination of the content of trace elements in the Devonian lavas (Fig. 3 and Table 4) shows that the latter contain the same assemblage of minor elements as the Cambrian lavas. Moreover, Devonian lavas show the same changes in the distribution of trace elements with increasing silica content of the rocks as do the Cambrian. The Devonian lavas differ from the Cambrian lavas in having a smaller content of trace elements. Table 4 shows that the Devonian lavas are poorer in the iron group of elements (except for Mn) as well as in the majority of minor elements. Only the gallium content is slightly higher in the Devonian than in the Cambrian extrusives. This agrees entirely with the conclusions reached by K. Rankama and Vorob'ev (1957) on the relative enrichment of younger extrusives in gallium.

Data on the chemistry of Devonian and Cambrian extrusives show a close similarity in chemical composition. The differences pointed out above and, in particular, the relative scarcity of femic minerals in the Devonian lavas and the enrichment of these minerals in iron at the expense of magnesium, may be explained by a more advanced stage of differentiation of the basaltic magma which gave rise to the Devonian lavas than of the magma which fed Cambrian volcanoes.

The basic conclusions drawn from the analysis of the chemistry of the investigated series of rocks may be briefly formulated.

1. Chemically the Cambrian extrusives are of the calc-alkalic type. They are derivatives of basaltic magma and belong to the spilite-keratophyre suite extruded during the early stages of formation of the Caledonian Tuvan geosyncline.

2. As a result of differentiation of the basaltic magma, lavas were formed ranging in composition from basalts to albitophyres and rhyolites. This process, however, did not follow the normal course of magmatic evolution entirely, and the general tendency of lavas to change in composition from mafic to felsic was complicated by alternation of lavas of varying degrees of maficity. This may be explained by the interrupted character of eruptive activity. After a period of dormancy in a local magmatic chamber,

products of advanced differentiation were erupted by a volcano first and
e followed by more mafic lavas tapped by deeper volcanic vents.
.   The Cambrian extrusives of Tuva are characterized by a definite as-
blage of trace elements which almost always contains the iron group of
ments and also copper, zinc, zirconium, gallium, strontium and barium.
regular variation in the trace element content during the process of
matic differentiation is characteristic. In the course of normal mag-
ic evolution the content of the iron group of elements and of gallium de-
ases, while the content of zirconium, strontium and barium increases.
.   A comparison of the chemistry of the Devonian and Cambrian lavas
uva indicates that both were derived from basaltic magma. The com-
tion of the Devonian lavas, however, reflects a more advanced stage of
erentiation of the parent magma. This situation is quite natural because
level of magmatic activity during the initial stages of development of the
donian Tuvan geosyncline was much lower than that which could be
hed by the Middle Paleozoic Tuva downwarp superimposed on the folded
ir basement.

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STRONTIUM IN THE GROUND WATERS
OF LOW SALINITY
IN THE MIDDLE PRE-URALS

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Hydrogeologically the middle pre-Urals may be divided into regions with different types of recharge and discharge of ground waters [1].

1. The region of water occurring in the joints of the principal and perched aquifers. This region is restricted to the areas of distribution of Ufimian and Solikamskian continental deposits. The waters are varied in composition, but carbonate waters with salinity up to 1000 mg/l predominate.

2. The karst region of water in solution openings and fractures. This region is restricted to the Artinskian and Kungurian carbonate and sulfate rocks. Notable among these waters are the dominantly calcium carbonate waters of the Filippovsk dolomites, often strongly charged with hydrogen sulfide. The karst waters in the gypsites at the base of the Iren'sk formation contain sulfates; their salinity is up to 3000 mg/l. In the upper part of this formation the impermeable Tuyisk limestones are overlain by sulfate karst waters with salinity from 1000 to 2000 mg/l.

3. The region of water occurring in the joints of the principal and perched aquifers in the Koshelevsk sandstones in the Kungurian continental deposits. The waters are of varied composition with salinity up to 2000 mg/l.

4. Calcium carbonate ground waters occur everywhere in the alluvium of large rivers (Ai, Ufa, Sylva, Irgina and others).

The investigaged part of the Uralian piedmont is composed mainly of Lower Permian deposits, which include carbonate rocks: limestones, marls and dolomites; sulfate rocks: anhydrites and gypsites; and clastic rocks: sandstones and conglomerates. The carbonate rocks predominate. Strontium occurs in all rocks, its content ranging from traces to 10% and more. The highest strontium content, over 10%, was found in the Artinskian carbonate rocks (Lemazinsk and Irginsk limestones). In the Kungurian formation there are several horizons with high strontium content. In the filippovsk formation, a series of brown-gray dolomites 10 m in thickness, has strontium content exceeding 1%. At the contact between the Filippovsk and Iren'sk formations, a white crystalline dolomite has a similar

Table 1

Stratigraphic horizon	Rocks	Number of samples	Salinity, mg/l	Average strontium content	
				in dry residue, %	in water mg/l
Q	Gravels, sands, clays	40	109–1752	0.28	2.29
P_1^{uf}	Sandstones	32	381–921	0.085	0.53
P_1^{sl}	Sandstones, marls, dolomites	11	256–1212	0.82	3.69
P_1^{3irn}	Anhydrites, gypsites, limestones, dolomites	10	293–2015	0.76	3.63
P_1^{3ks}	Sandstones, marls	4	318–781	1.0	3.85
P_1^{3phl}	Dolomites, limestones	9	532–1708	0.70	5.50
P_1^{2lem}	Limestones	8	310–1729	1.0	6.23
D	Limestones	15	31–279	0.003	0.004

strontium content. High strontium content marks also the contact between gray dolomite and bluish-gray anhydrite (Shalashinsk beds) and the Elkinsk dolomites with anhydrite inclusions. A relatively high strontium content is found in similar rocks of the Demidkovsk and Lunezhsk beds. The form of occurrence of strontium in the Lower Permian deposits is not known.

Water samples for hydrochemical investigation of strontium and other minor elements were taken from springs, wells and boreholes. Altogether, 189 dry residues were analyzed.

Strontium was determined on the ISP-22 spectrograph by the roughly quantitative method of comparison spectra. The standards were prepared with the base corresponding to the average composition of ground waters of the region under investigation. The composition of the base in mg/l was as follows: HCO_3 -- 366.0, Cl -- 43.4, SO_4 -- 148.0, Mg -- 12.0, Ca -- 174.6, Na – K -- 19.4; its salinity -- 759.4 mg/l.

Standards with strontium content of 1.0, 0.1, 0.01, 0.001% were prepared by the method of dilution. To insure that the same volume of material was used in each analysis, the samples and the standards were vaporized in the cavity of the lower electrode. The electrodes were copper. The arc was activated with a current of 6.5-7 amps. The spectrum of the sample was photographed between the spectra of the standards. The comparison of the intensity of strontium lines 4077.714 A and 4607.331 A was made visually with the aid of a spectrum projector. The analyses were made by A.M. Kropachev.

The results show that the strontium content in the dry residues varies from zero to 1% and more.

Table 2

Age of rocks	Sampling locality	Salinity, mg/l	Anions, mg/l			Cations, mg/l			Strontium content	
			HCO₃	Cl	SO₄	Mg	Ca	Na+K	%	mg/l
Q	Village of Strashnaya, well	1098,3	552,0	170,5	71,7	9,05	282,4	12,4	0,05	0,54
»	Village of B. Savino, well	712,9	488,0	0,05	47,8	5,5	166,2	6,4	0,01	0,07
»	Village of M. Burtym, well	316,2	244,0	3,48	—	17,7	52,8	0,18	1,0	3,16
»	Village of Filatovo, well	879,4	347,7	64,6	16,0	17,32	128,4	0,23	0,01	0,09
»	Village of Khlopushi, well	742,9	378,2	124,2	43,2	31,0	157,4	7,36	0,1	0,74
»	Village of Ermashi, well	618,8	402,6	38,34	16,0	9,4	93,4	59,11	0,01	0,06
»	Village of Mart'yanovo, well	431,0	280,6	24,85	20,0	12,57	92,4	1,38	1,0	4,31
p_1^{uf}	Village of Paderino, well	523,9	305,0	49,7	32,6	3,39	125,2	1,38	1,0	5,24
»	Village of Shimyaki, well	622,9	366,0	63,8	31,2	3,66	136,6	31,0	0,01	0,06
»	Village of Soboli, spring	453,8	292,8	10,3	4,0	40,26	98,8	7,71	1,0	4,51
»	Village of Palitsy, well	669,5	439,2	25,85	16,0	26,23	157,4	4,83	0,1	0,66
p_1^{3irm}	Village of Golyshevo, spring	1854,3	243,0	24,8	1046,4	2,7	449,6	87,8	>0,1	1,85
P_1^{3phl}	Village of Zasekino, well	578,5	329,4	72,0	14,2	2,8	145,0	9,7	1,0	5,78
»	Village of Frolovo, well	720,6	378,2	7,2	125,6	19,4	165,4	24,84	1,0	5,71
»	Village of Azhbaevo, well	532,4	341,6	7,2	48,0	3,12	121,0	11,5	1,0	5,32
»	Village of Fedotovo, well	795,8	524,0	28,5	38,5	3,5	177,8	23,5	1,0	7,95
»	Saya River, source	1708,3	244,0	28,4	944,6	5,7	448,8	36,8	>1,0	17,08
»	Village of Komarovo, well	844,9	430,0	39,0	148,4	2,7	201,2	23,5	>1,0	0,84

Note: Comma represents decimal point.

Samples with strontium content between 0.1 and 1.0% in the dry residues predominate (1-5 mg/l in water).

The distribution of strontium in the waters of different stratigraphic horizons of the investigated regions is irregular. High strontium content is found in the Kungurian deposits, in the carbonate rocks of the Solikamsk and Filippovsk formations and also in the Lemazinsk limestones of the Artinskian stage. Low strontium content characterizes the waters of the Upper Permian Ufimian stage and the Devonian carbonate rocks (Table 1).

The irregular distribution of strontium in the waters of different stratigraphic horizons is due to the difference in its content in the rocks of these horizons. The high strontium content in the waters of the Iren'sk, Filippovsk and Lemazinsk formations is due to the high content of the element in these rocks. The high strontium content in the waters coming to the surface in the region of the Koshelevsk sandstones is due to the fact that the chemical character of these waters was formed mainly in the strontium-rich Iren'sk carbonate and sulfate rocks, outside of these sandstones, which are poor in strontium (0.007% on average). The strontium-rich rocks lie to the west of the continental deposits.

The cause of the high strontium content in the waters of the Solikamsk deposits is not clear at present, since there are no data on the distribution of strontium in these rocks. The waters of the Devonian beds were studied in the Chusovsk region. In the neighboring Kizelovsk region the Devonian carbonate rocks have a low strontium content, not exceeding 0.05%. If the Devonian carbonate rocks of the Chusovsk region are as low in strontium, the low strontium content in the waters of Devonian deposits must be ascribed to its low content in the rocks.

In their low strontium content, which averages 0.0031%, the ground waters of the middle pre-Urals resemble marine waters containing 0.0013% Sr on average [2]. The dry residue of sea water contains 0.015% Sr; the dry residue of the ground waters of the pre-Urals, 0.46%. Thus the waters of the pre-Urals are somewhat more saturated with strontium than the marine waters, which are not saturated with it. As compared with the oil field waters of the pre-Urals, which contain from 275 to 892 mg/l Sr, the ground waters of this region are much poorer in strontium.

Most of the investigated waters are of calcium carbonate and calcium sulfate type. Chemical analyses of waters from different stratigraphic horizons are given in Table 2.

The relatively high strontium content in ground waters is due to its water soluble state in the rocks. In a temperate forest zone strontium is a "water migrant" [3]. It is easily leached out of soils and rocks, and enters ground water. It has been pointed out by A. P. Vinogradov [4] that podzols lose strontium and heavy metals. It is probable that in ground waters strontium migrates in true solution, for the abundance of calcium, a strong coagulator of colloids, makes it almost impossible for the substance to migrate in the colloidal state.

Our work has shown that strontium is widely distributed in the ground waters of the pre-Urals. Relatively high strontium content, up to 26 mg/l, was found in the Permian deposits, which are abundantly represented in the southeastern part of the Perm region.

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BIOGEOCHEMICAL SURVEYS
IN PROSPECTING FOR URANIUM
IN MARSHY AREAS

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The work done on the use of biogeochemical surveys in the search for uranium, by N.V. Kvashnevskaya (1948), N.N. Sochevanov (1950) [1] and D.P. Malyuga [2] in the Soviet Union and by other workers abroad [3, 4, 5, 6], indicates that the method has possibilities in locating uranium deposits.

So far, the biogeochemical method has not been used in prospecting for uranium in the marshy areas of the taiga (Siberian forests). In order to determine its effectiveness under these conditions, experimental work was done in the European part of the USSR.

The investigations were made over an area 0.25 km to 0.5 km wide and 2.5 km long. A number of ridges occur in the area. Between the ridges are flat, locally marshy depressions. The area is covered with a mixed spruce-birch forest, spruce being strongly predominant. There are also pine, willow, alder, poplar, buckthorn and chokecherry. Among the herbs, sedge is predominant, and large areas are covered with mosses.

Experiments were conducted in areas where soils showed relatively high radioactivity and over known ore bodies. Biogeochemical surveys were made also in areas which had given negative radiometric results but where ore could be expected under thick, water-saturated overburden (moraines).

Needles, leaves and other exposed parts of herbs and mosses were selected for analysis. In some cases, twigs and roots were collected at the same time for comparison. At a number of points, samples of different plants were taken to determine uranium concentrators among them. The samples were collected mainly along the lines of an exploration grid so that they could be marked exactly on the geologic map and the results of the survey comapred with the results obtained by other methods. The uranium content in the plant ash was determined by the fluorescence method.

According to the literature [2, 7], the average uranium content in plants is from $n \times 10^{-6}$ to $5 \times 10^{-5}\%$ (in ash). Most of the 1105 plant samples collected in the area contain from 1×10^{-4} to 5×10^{-4} uranium, i.e., considerably more than the average. This constitutes the local geochemical uranium background. Uranium content greater than $5 \times 10^{-4}\%$ was considered anomalous for the area. It was found in the ashes of only seventy samples, i.e., in 6.5% of the total number of samples. A list of these samples is given in the table.

Uranium Content in Plants and in the Soils
in Which They Grew

Name of Plant	Uranium content in plant ash, $n \times 10^{-4}\%$	Uranium content in soil, $n \times 10^{-4}\%$
1	2	3
Mosses		
Moss -- Scorpidium scorpioides, fam. Hypnaceae	189	244
"	155	65
"	136	46
Moss -- Calliergon giganteum, fam. Hypnaceae	115	38
"	101	38
"	94	39
"	57	156
Moss -- Drepanocladus fluitans, fam. Hypnaceae	54	65
"	41	58
"	33	59
"	19	13
Moss -- Polytrichium commune, fam. Polytichaceae	19	15
"	14	34
"	14	1
"	11	8
Sphagnum centrale, fam. Sphagnaceae	9	20
"	9	3
"	7	46
"	6	4
"	6	49
Herbs		
Sedge -- Carex caespitosa, fam. Cyperaceae	99	244
"	71	179
"	56	156
"	41	3
"	33	54
"	28	150
"	24	16
"	10	300
"	9	300
"	7	170
Aegopodium podagraria L., fam. Umbeliferae	67	110
"	53	208
"	33	366
"	21	78

Table (Cont'd.)

Uranium Content in Plants and in the Soils
in Which They Grew

Name of Plant	Uranium content in plant ash, $\underline{n} \times 10^{-4}\%$	Uranium content in soil, $\underline{n} \times 10^{-4}\%$
1	2	3
Ground pine -- <u>Lycopodium annotinum</u> L., fam. Lycopodiaceae	20	16
"	19	204
"	15	202
Filipendula ulmaria Maxim., fam. Rosaaceae	11	29
"	10	19
Crepis paludosa Moench., fam. Compositae	9	1600
"	7	49
"	7	28
Silver top -- <u>Deschampsia caespitosa</u> P.B., fam. Gramineae	7	15
"	7	34
Heal All -- <u>Prunella vulgaris</u> L., fam. Labiatae	7	29
"	6	55
Monkshood - <u>Aconitum excelsum</u> Rchb., fam. Ranunculaceae	6	3
Trees		
Spruce -- <u>Picea excelsia</u> Zenk, fam. Pinaceae (needles)	400	8
" (needles)	16	63
" (root)	10	7
" (stem)	6	10
" (root)	9	29
" (stem)	7	10
" (root)	7	8
" (stem)	7	7
" (needles)	6	7
" (needles)	6	48
" (needles)	6	5
" (needles)	6	8
Buckthorn - <u>Frangula alnus</u> Mill, fam. Rhamnaceae (leaves)	36	41
Alder -- <u>Alnus incana</u> Willd, fam. Betulaceae (leaves)	43	33
"	7	6
"	6	6

Table (Cont'd.)

Uranium Content in Plants and in the Soils
in Which They Grew

Name of Plant	Uranium content in plant ash, $\underline{n} \times 10^{-4}\%$	Uranium content in soil, $\underline{n} \times 10^{-4}\%$
1	2	3
Willow – Salix caprea L., fam.		
Salicaceae (leaves)	400	245
"	9	40
"	6	7
"	6	9
Birch – Betula pubescens Ehrh., fam.		
Betulaceae (leaves)	6	28
"	6	7
Sorbus aucuparia L., fam.		
Rosaceae (leaves)	6	9

The table shows that soils usually contain more uranium than plants. Only eighteen plant samples had higher uranium content than the soils. Eleven of these were mosses and the rest samples of sedge, spruce and alder. It should be noted that the high uranium content in soil does not always indicate high uranium content in plants. Sometimes when the uranium content in humus is 0.1%, its amount in the plants collected from these enriched soils is less than $5 \times 10^{-4}\%$. The same relationship was observed between plant samples and alluvium. For example, at a number of points with the uranium concentration in alluvium exceeding $50 \times 10^{-4}\%$, its content in the plant samples was no more than the average.

To discover plant concentrators of uranium, the uranium content in the ash of different plants collected in a given area was measured. The results show that moss concentrates more uranium than the associated grasses and trees. The trees (willow, spruce, etc.) contain less uranium than the herbs (sedge, various weeds).

Summary

The results of the investigation show that biogeochemical prospecting for uranium is feasible in the marshy areas of the taiga by using soils and plants. The uranium concentration in plants is lower, as a rule, than in the soils, and in searching for uranium in marshy areas, examination of soils must be given preference.

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PROFESSOR F. A. PANETH

Professor F.A. Paneth died in Vienna on September 17, 1958. He was born in Vienna in 1887 but spent a considerable part of his life in other cities of Europe.

Paneth's scientific activity began in the Vienna Radium Institute at the dawn of the development of radiochemistry. In 1912-1914, he worked with natural isotopes and was the first to use them as tracers in physicochemical experiments. With the aid of tracers, he determined the solubility of difficultly soluble salts and the distribution of trace elements between two phases, discovered the existence of radiocolloids, utilized radon for the determination of specific surface of porous bodies and of the passage of gases through a carbon screen.

In those days, F.A. Paneth was one of the few who understood the future scientific and practical importance of radioactive isotopes. He considered radiochemistry, a new field of knowledge, as chemistry of substances which are detected by their nuclear radiations. This concept enters into the modern definition of radiochemistry. A broadly educated chemist, he was connected with many universities in Germany and other countries. Both in radiochemistry and in other fields in which he worked (for example, in his study of free radicals of inert gases), Paneth's researches were distinguished by exceptional precision of technique. This is true also of his geochemical and cosmochemical investigations, for example, his measurements of the age of iron meteorites by the helium method, of the radioactivity of rocks and meteorites, etc. Working in this direction, he created a school.

These researches were made after he left Germany in 1933 and settled first in London and, somewhat later, in Durham. Here, as a result of careful investigations, he obtained the first data on the age of iron meteorites, using the U/Th--He method. Later, he made mass-spectrometric studies of the inert gases in the atmosphere and in meteorites and of the He^4/He^3 ratio.

In 1953, Paneth returned to the German Federal Republic to the Mainz Academy of Sciences. In recent years he was more and more attracted by geochemical and cosmochemical problems. He participated in a number of international committees and numerous scientific Conferences.

Many Soviet scientists knew Paneth personally. I saw him for the last time in Paris in 1957 at the conference on the use of radioactive isotopes in scientific investigations, where he took part in the discussions of cosmochemistry and meteoritics. He was an erudite scientist, a profound investigator gifted with philosophical penetration. His researches in radiochemistry,

geochemistry of the inert gases and determination of the absolute age of meteorites have influenced the development of geochemistry and cosmochemistry and the work of the new generation of scientists.

A. P. Vinogradov

Geokhimiya began publication in 1956 under the able editorship of A. P. Vinogradov. It is the Soviet counterpart of Geochimica et Cosmochimica Acta, having practically identical fields of interest and coverage and publishing approximately the same number of pages per year. With the great increase in geochemical research in the U. S. S. R., there have come into being a number of highly specialized journals in geochemistry and related fields. It is probably better to begin translating this more general journal first and follow with some of the more specialized ones if interest appears to justify this course of action and if the financial arrangements can be made.

An initial grant from the National Science Foundation in 1958 enabled the Geochemical Society to translate and publish the eight issues for that calendar year. These issues have been very well received by a growing list of subscribers in most of the countries of the Western world.

Many inquiries have been received concerning back issues (1956 and 1957) and continuation of the program for issues after 1958. The National Science Foundation has made additional grants for translation and publication of the issues for 1956, 1957 and 1959. These are being translated and issued as rapidly as they can be processed. Prices are the same as for the 1958 issues (see inside front cover). Subscriptions and orders for single copies should be sent to the Geochemical Society in care of the undersigned.

The National Science Foundation has continued to be most cooperative in this venture. They are continuing support of the project although subscriptions are too few to make it anything like self supporting thus far. It is hoped that subscribers will call attention of other interested workers to the availability of the translation of Geokhimiya so that these important research papers can be made more generally available to those interested in geochemical and related investigations.

<div style="text-align:right">

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Geochemical News is an informal bi-monthly newsletter published by the Geochemical Society and sent without charge to all of its members. It contains news of the activities of the Society, such as summaries of Council Meetings, reports of committees and plans for the future. It also includes announcements of forthcoming meetings and symposia of interest to geochemists, personalia, announcements or short reviews of books of geochemical interest, information on translations and translation services, letters and short notes by members, etc.

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New chemical data and interpretations involving chemical principles are emphasized. For example, papers in chemical mineralogy, petrology, oceanography and volcanology are acceptable, as are those in the chemistry of meteorites, whereas it would be suggested that those in descriptive mineralogy and volcanology, petrography, physical and biological oceanography and physical meteoritics, be sent to other journals specializing in these subjects.

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